Acid-Catalyzed Conversion of 7-Ethynyl- and 7-Vinylcyclohepta-1,3,5-trienes to Substituted Benzene Derivatives

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The acid-catalyzed rearrangement in THF/TFA (5:1, v/v) of cyclohepta-1,3,5-trienes containing an α,β -unsaturated substituent at C-7 was investigated. 7-Ethynylcyclohepta-1,3,5-triene (**1a**) and its 1,4-di-*tert*-butyl (**1b**), 1,5-di-*tert*-butyl (**1c**), and 2,5-di-*tert*-butyl (**1d**) derivatives underwent isomerization to phenylallenes **2**, **3**, **7**, and **3**, respectively. 2,5-Di-*tert*-butyl-7-vinylcyclohepta-1,3,5-triene (**17**) gave a mixture (66:34) of (*E*)- and (*Z*)-1,4-di-*tert*-butyl-2-(1-propenyl)benzene (**20**). A mechanism involving the protonation of the norcaradiene tautomer (NCD), which is in equilibrium with cycloheptatriene (CHT) **1** or **17**, followed by the cleavage of a three-membered ring to give an arenium ion, is proposed. In contrast, 2,5-di-*tert*-butyl-7-cyanocyclohepta-1,3,5-triene (**12**) and bis(cyclohepta-2,4,6-trien-1-yl)ethyne (**21**) did not

Introduction

Although several investigations regarding the reactions of 7-ethynylcyclohepta-1,3,5-triene (1a) have been reported, including, for example, complex formation with transition metals^[1,2] and conversion into the corresponding tropylium ion,^[2] no reports concerning the possibility of the rearrangement of this compound under acidic conditions have appeared. In a preliminary communication,^[3] we reported the clean conversion of **1a** into phenylallene **2** in the presence of acid (Scheme 1). The reaction was found to be sufficiently rapid that it occurs without any significant ther-



Scheme 1

give the expected products, probably due to the unfavorable energetics of the ring-opening step. A thermal 1,5-hydrogen shift predominates in these cases. Kinetic studies indicated that the rearrangement of **1a** is significantly accelerated by the presence of *tert*-butyl groups on the seven-membered ring. The order of reactivity, **1a** < **1b** < **1c** < **1d**, is in agreement with the population of NCD forms at equilibrium, as estimated by the calculated CHT–NCD energy-difference and the ¹³C NMR chemical shifts of **1a–d**, indicating the importance of the equilibrium concentration of the norcaradiene form as a rate-controlling factor.

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mal 1,5-hydrogen shift, a reaction which is normally observed for cyclohepta-1,3,5-trienes at temperatures higher than 100 $^{\circ}$ C.^[4]

The acetylene–allene rearrangement^[5–9] is known to be catalyzed both by base and acid, but reports of isomerization in acidic media^[10] have been rather few. A possible explanation for this is that due to the reversible nature of the rearrangement under acidic conditions, the product is frequently a mixture of the desired allene and isomeric acetylenes. In contrast, the rearrangement of **1a** to **2** is irreversible, because of the formation of an aromatic ring.^[3]

The clean rearrangement of **1a** suggests the possibility of analogous acid-catalyzed conversions of other cyclohepta-1,3,5-trienes bearing directly attached multiple bonds into benzene derivatives. In this paper we report the reaction of cyclohepta-1,3,5-trienes containing an ethynyl, vinyl, or cyano group at C-7.

Results and Discussion

Acid-Catalyzed Rearrangement of 7-Ethynylcyclohepta-1,3,5-trienes

Heating 7-ethynylcyclohepta-1,3,5-triene (1a) and its *tert*butyl-substituted derivatives 1b-d at 60 °C in a mixture of THF and trifluoroacetic acid (TFA) (5:1, v/v) gave the substituted benzene derivatives in nearly quantitative yields

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(Table 1). The rearrangement of **1a** and **1d** gave phenylallenes **2** and **3**, respectively, as the sole products. A plausible pathway, shown in Scheme 2, includes an initial cycloheptatriene (CHT)-norcaradiene (NCD) equilibrium.^[11-13] The three-membered ring of the protonated form of the NCD tautomer **4** can be cleaved to give an arenium ion intermediate **5**, which on deprotonation gives phenylallene **2** or **3**.



Table 1. TFA-catalyzed rearrangement of 7-ethynylcyclohepta-1,3,5-trienes $1a\!-\!d^{[a]}$

	Substituents on sp ² C atoms	Time [h] ^[b]	Product
1a	none	960	2
1b	1,4-(<i>t</i> Bu) ₂	24	3 + 6 (68:32)
1c	1,5-(<i>t</i> Bu) ₂	24	7 + 8 (93.4:6.6)
1d	2,5-(<i>t</i> Bu) ₂	3	3

^[a] In THF/TFA (5:1, v/v), at 60 °C. ^[b] The reaction times correspond to 4-6 half lives of the consumption of the starting compound.





Similarly, the rearrangement of **1b** and **1c** gave (di-*tert*butylphenyl)allenes **3** and **7**, respectively (Scheme 3), which are the products expected by similar mechanisms (Scheme 4). In each case a phenylallene with a single *tert*butyl group (**6** or **8**) was also produced as a minor product. The formation of **6** and **8** can be explained by the cleavage of the C–C bond of the three-membered ring by route b, followed by elimination of a *tert*-butyl cation. The large difference between the yields of the two products (93.4:6.6) for the reaction of **1c** can be attributed to the large difference in energy between the arenium ion intermediates **9** and **10**. The 2,4-pentadien-1-yl cation moiety of **9** is effectively stabilized by the two *tert*-butyl groups at C-1 and C-5, where the positive charge is expected to be largely distributed. In





contrast, the pentadienyl cation moiety of **10** contains only one *tert*-butyl group at C-2, where the distribution of the positive charge should be small.

In an attempt to trap the intermediate cationic species, the rearrangements of 1a and 1d were carried out at 60 °C in methanol, containing 0.50 м HCl.^[14] Both compounds rearranged much faster in this system than in THF/TFA, and the same products as those obtained in THF/TFA (2 and 3, respectively) were formed quantitatively in 3 h. The failure to trap the cationic intermediates by methanol or chloride ion can be attributed to the rapid rearrangement of the vinyl cation 4 to arenium ion 5, followed by immediate deprotonation to form an aromatic ring. Such a rearrangement would be thermodynamically favorable due to the release of the strain of the cyclopropane ring in 4 and the resonance stabilization of 5. DFT calculations [B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) indicated that the most stable form of 4 (R = H) has an *exo* configuration, and 5 (R = H) favors a conformation with the allenvl group *anti*orientated with respect to the six-membered ring. The latter has been shown to be more stable than the former by 3.69 kcal·mol⁻¹ (Figure 1).

An alternative pathway for the formation of dealkylation products 6 and 8 is the acid-promoted elimination of a *tert*butyl cation from 3 and/or 7 (Scheme 5), which may form the mono-*tert*-butyl derivatives 8 and 11. The migration of the other *tert*-butyl group in these products can yield 6. However, these possibilities were ruled out by control experiments, in which heating 3 and 7 under the same conditions for 24 h resulted in the quantitative recovery of the starting materials. No dealkylation product (6, 8, or 11) was detected, which is consistent with the formation of these products by the mechanism shown in Scheme 4.

Acid-Catalyzed Rearrangement of 7-Cyano- and 7-Vinylcyclohepta-1,3,5-trienes

7-Cyanocyclohepta-1,3,5-trienes may be regarded as nitrogen analogs of 7-ethynylcyclohepta-1,3,5-trienes, and are expected to undergo a similar rearrangement under acidic conditions to give keteneimine derivatives such as **15**



Scheme 4



Figure 1. Optimized structures and relative energies of the intermediate cations 4 (R = H) and 5 (R = H) obtained by the B3LYP/ 6-311+G(2d,p)//B3LYP/6-31G(d) level of theory



electron-withdrawing substituent at C-7 is known to effectively shift the CHT-NCD equilibrium toward the NCD side.[15-17] However, the attempted acid-catalyzed rearrangement of 12 in THF/TFA (5:1, v/v) at 100 °C for 50 h resulting in the complete conversion of starting material to a multi-component mixture, in which no aromatic compound was detected. The ¹H NMR spectrum of the reaction mixture showed signals at $\delta = 2.23$ (d, J = 8.0 Hz) and $\delta = 5.49$ (t, J = 8.0 Hz) ppm with a 2:1 intensity ratio. These signals can be assigned to 7-H and 6-H of 16, respectively. Thus, it appears that a thermal 1,5-hydrogen shift to form 16 has predominated over any acid-catalyzed rearrangement. Protonation of the norcaradiene tautomer of 12 forms a resonance-stabilized cation $13a \leftrightarrow 13b$, which makes ring opening to arenium ion 14 energetically unfavorable. DFT calculations [B3LYP/6-311+G(2d,p)//B3LYP/ 6-31G(d)] indicated that 14 is higher in energy than 13 by $3.00 \text{ kcal} \cdot \text{mol}^{-1}$.

(Scheme 6). This transformation may be more favorable than the rearrangement of 7-ethynyl derivatives, because an



On the other hand, 7-vinylcyclohepta-1,3,5-triene 17 cleanly rearranged in THF/TFA (5:1, v/v) at 60 °C to give (1propenyl)benzenes (*E*)-20 and (*Z*)-20, which were separable

Scheme 5

14



15

Scheme 6



Scheme 7

by HPLC (SiO₂), in an isomer ratio of 66:34 (Scheme 7). Heating isolated (*E*)-20 and (*Z*)-20 under the same conditions for 24 h showed no evidence of (E)/(Z) isomerization. This indicates that the observed (*E*)-20/(*Z*)-20 ratio is the result of the kinetically controlled opening of the three-membered ring of 18 to isomers of 19.



The clean rearrangements of 7-ethynyl- and 7-vinylcyclohepta-1,3,5-trienes led us to expect that bis(cyclohepta-2,4,6-trien-1-yl)ethyne (21) would undergo a similar acidcatalyzed rearrangement to initially form an allene 22. The other cycloheptatrienyl group of this compound would further rearrange to eventually give diphenylbutadiene (24) (Scheme 8). Heating of 21 at 100 °C for 50 h in THF/TFA (5:1, v/v), however, gave only a complex mixture (> 7 components) of unidentified products. The NMR analysis of the mixture indicated the formation of aromatic products, but 24 was not detected.^[18] A possible explanation for this result is that the rearrangement of the second cycloheptatrienyl group (i.e. from 22 to 24) is difficult, since the opening of the three-membered ring of cation 23 is energetically unfavorable due to delocalization of the positive charge over the 3-phenylallyl group. The initial product 22, if produced, appears to be consumed by thermal 1,5-hydrogen shifts to form isomers of 22 that are inert to acid-catalyzed rearrangement.



Scheme 8

Rate Studies

The rate of the acid-catalyzed rearrangement of 7-ethynylcyclohepta-1,3,5-trienes 1a-d is largely dependent on the number and position of the *tert*-butyl substituents. For the kinetic study, the reaction was conducted in [D₈]THF/TFA (5:1, v/v) by using an NMR sample tube. The progress of the reaction was monitored by integration of the ¹H NMR peaks. The decay of the starting compounds followed the first-order kinetics. The obtained rate constants are listed in Table 2.

Table 2. Rate constants (k_1) for acid-catalyzed rearrangement, ¹³C chemical shifts (δ), and calculated energy of the conformers/isomers of **1a**-**d**

	$k_1^{[a]}$ [10 ⁻⁶ s ⁻¹]	δ(C-6) ^[b] [ppm]	Relative energy ^[c] [kcal·mol ⁻¹]
1a	0.879	122.7	2.75 (<i>ax</i> -CHT) 0.00 (<i>eq</i> -CHT) 6.62 (<i>endo</i> -NCD) 4.65 (<i>exo</i> -NCD)
1b	28.6	117.7	0.00 (<i>ax</i> -CHT) 0.81 (<i>eq</i> -CHT) 4.13 (<i>endo</i> -NCD) 5.13 (<i>exo</i> -NCD)
1c	46.8	102.5	0.00 (<i>ax</i> -CHT) 0.41 (<i>eq</i> -CHT) 3.79 (<i>endo</i> -NCD) 4.57 (<i>exo</i> -NCD)
1d	322	91.5	3.47 (<i>ax</i> -CHT) 0.00 (<i>eq</i> -CHT) 3.44 (<i>endo</i> -NCD) 1.17 (<i>exo</i> -NCD)

^[a] In $[D_8]$ THF/TFA (5:1, v/v), at 60 °C. ^[b] In CDCl₃, 23 °C. ^[c] Obtained at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level.

Thermal CHT–NCD equilibrium is a key step in the mechanism of this rearrangement, as shown in Schemes 2 and 4. Although unsubstituted cyclohepta-1,3,5-triene is far more stable than norcaradiene, the energy level of the CHT form is known to be increased by the introduction of bulky substituents to the olefinic carbon atoms.^[19–22] For example, 2,5-di-*tert*-butyl-7-ethynylcyclohepta-1,3,5-triene (**1d**) is known to exist as an equilibrium mixture of CHT and NCD in a ratio 79.5:20.5.^[22]

The energies calculated for the four conformers/isomers of 1a-d (Scheme 9) indicated that the most stable forms are *eq*-CHT for **1a** and **1d** and *ax*-CHT for **1b** and **1c** (Table 2). The increased energy of the *eq*-CHT conformers of **1b** and **1c** relative to the axial forms may be due to steric repulsion between the 7-ethynyl group and the 1-*tert*-butyl group. The most easily accessible NCD isomers are *exo* for **1a** and **1d** and *endo* for **1b** and **1c** for a similar reason. The difference in energy between CHT and NCD is 4.65 kcal·mol⁻¹ for **1a**. This value is only slightly lower than the reported CHT-NCD free energy difference of 5.6 kcal·mol⁻¹ obtained for unsubstituted cyclohepta-1,3,5triene by the HF/6-31G(d) level.^[23] The CHT-NCD energy



Scheme 9. Valence isomers and conformers of 7-ethynylcyclohepta-1,3,5-triene 1 and its norcaradiene form

gap (kcal·mol⁻¹) decreased in the order 1a (4.65) > 1b (4.13) > 1c (3.79) > 1d (1.17).

The increase in the fraction of the norcaradiene form can be also estimated by the ¹³C NMR chemical shifts. The chemical shifts for C-1 and C-6 serve as indicators for the position of the CHT-NCD equilibrium, because these carbons change their orbital hybridization from sp² to sp³ upon transformation from CHT to NCD. Due to rapid tautomerization at room temperature, these carbon atoms show a time-averaged signal between the aliphatic and the aromatic regions. Assuming that the influence of the group attached at C-5 (H or tBu) is negligible, the observed C-6 chemical shifts $\delta(C-6)$ reflect the position of equilibrium. The chemical shift data in Table 2 show that the population of the norcaradiene form increases in the order 1a < 1b< 1c < 1d, in agreement with the DFT calculations. This tendency parallels the order of the rate constant, indicating that the CHT-NCD composition at equilibrium is closely related to the reactivity toward the acid-catalyzed rearrangement.

Conclusion

7-Ethynyl- and 7-vinyl-substituted cyclohepta-1,3,5trienes were found to undergo clean rearrangement to form phenylallene and (1-propenyl)benzene derivatives respectively, under acidic conditions. The rearrangement of 7ethynylcyclohepta-1,3,5-triene (**1a**) is very slow (half life of 9 d at 60 °C in THF/TFA, 5:1, v/v), but is still sufficiently rapid so as to occur without any significant thermal 1,5hydrogen shift. This slow rate can be attributed to the very low concentration of the norcaradiene form at CHT–NCD equilibrium, but a significant acceleration was observed when *tert*-butyl groups were introduced, which shifted the equilibrium to the NCD side. Ring-opening of the threemembered ring of the norcaradiene structure should be energetically favorable for a clean acid-catalyzed rearrangement to be realized. This requirement somewhat limits the scope of the present transformation, as illustrated by the cases of cyano- and allenyl-substituted cyclohepta-1,3,5-trienes, where side-reactions such as thermal 1,5-hydrogen shifts override the acid-catalyzed rearrangement.

Experimental Section

General: ¹H and ¹³C NMR spectra were obtained with JEOL-EX400 (¹H, 400 MHz; ¹³C, 100 MHz), AL300 (¹H, 300 MHz; ¹³C, 75 MHz), and GSX270 (¹H, 270 MHz; ¹³C, 68 MHz) spectrometers. Peak assignments are based on DEPT, COSY, and H–C COSY measurements. High-resolution mass spectra were obtained with JEOL JMS-HX110 and JMS700 mass spectrometers. Gel permeation chromatography (GPC) was performed using a Japan Analytical Industry JAIGEL 1H+2H polystyrene columns with chloroform as the eluent. Tropylium tetrafluoroborate^[24] and 1,4di-*tert*-butyltropylium perchlorate^[25] were synthesized by previously reported methods. THF was purified by distillation from benzophenone ketyl prior to use. DFT calculations were performed using the Gaussian 98 program.^[26] Geometry optimizations were verified by frequency calculations.

7-Ethynylcyclohepta-1,3,5-triene (1a): Acetylene gas (passed through H_2SO_4) was introduced into a graduated test tube containing 10 mL of THF at -66 °C until the volume of the solution increased by 6.4 mL. The collected acetylene [approximated as 4.5 g (0.17 mol) assuming a density of 0.7 g mL⁻¹ ^[27]] in THF was transferred through a cannula to a four-necked flask containing 50 mL of THF at -66 °C. A 1.38 mol·L⁻¹ solution of BuLi in hexane (12.0 mL, 0.0166 mol) was added dropwise over 20 min. Tropylium tetrafluoroborate (3.04 g, 0.0171 mol) was added, and the mixture was stirred at 0 °C for 90 min. After the solvent had been evaporated, the residual brown oil was purified by GPC to afford 7-ethynylcyclohepta-1,3,5-triene (1a, 1.35 g, 68%) and bis(cyclohepta-2,4,6-trien-1-yl)ethyne (21, 99 mg, 5.6%).

1a: Pale-yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 2.15 (d, *J* = 2.4 Hz, 1 H, ≡CH), 2.49 (br. s, 1 H, 7-H), 5.32 (m, 2 H, 1,6-H), 6.15 (m, 2 H, 2,5-H), 6.62 (m, 2 H, 3,4-H) ppm. ¹³C NMR (68 MHz, CDCl₃): δ = 31.3 (C-7), 68.4 (≡CH), 85.5 (−*C*≡CH), 122.7 (C-1,6), 124.8 (C-2,5), 130.9 (C-3,4) ppm. IR (neat): \tilde{v} = 3303 (≡C−H), 2126 (C≡C) cm⁻¹. The ¹H NMR spectroscopic data are in agreement with previously reported data.^[28]

Di-tert-butyl-7-ethynylcyclohepta-1,3,5-trienes 1b-d: A mixture of isomers of di-*tert*-butyl-7-ethynylcyclohepta-1,3,5-trienes was obtained by the addition of 1,4-di-*tert*-butyltropylium perchlorate (3.09 g, 10.2 mmol) to a THF solution (110 mL) of ethynyllithium (12.1 mmol) by a procedure similar to that employed for the synthesis of **1a**. Separation by MPLC (SiO₂, hexane) gave a fraction containing pure **1d** (0.46 g, 20%) and one (1.85 g) containing **1b** and **1c**. A portion (0.88 g) of the latter fraction was further separated by HPLC (Waters µPorasil, hexane) to give **1b** (0.30 g, 27%) and **1c** (0.51 g, 46%).

1,4-Di-*tert*-**butyl-7-ethynylcyclohepta-1,3,5-triene** (1b): Colorless crystals, m.p. 84.5−86.5 °C. ¹H NMR (270 MHz, CDCl₃): δ = 1.18 (s, 9 H, *t*Bu), 1.20 (s, 9 H, *t*Bu), 1.68 (br. s, 1 H, ≡CH), 3.97 (br. s, 1 H, 7-H), 5.43 (t, *J* = 9.3 Hz, 1 H, 6-H), 6.07 (d, *J* = 6.7 Hz, 1 H, 2-H), 6.30 (d, *J* = 9.3 Hz, 1 H, 5-H), 6.54 (dd, *J* = 6.7, 1.2 Hz, 1 H, 3-H) ppm. ¹³C NMR (68 MHz, CDCl₃, 60 °C): δ = 29.0 (C-7), 29.7 (CH₃), 30.2 (CH₃), 35.6 [*C*(CH₃)₃], 36.2 [*C*(CH₃)₃], 66.4

(=CH), 83.4 (-C=CH), 117.0 (C-6), 118.7 (C-2), 123.4 (C-3), 125.6 (C-5), 141.9 (C-1 or C-4), 150.1 (C-1 or C-4) ppm. IR (KBr): $\tilde{v} = 3278$ (=C-H) cm⁻¹. C₁₇H₂₄ (228.37): calcd. C 89.41, H 10.59; found C 89.16, H 10.42.

1,5-Di-*tert*-**butyl-7-ethynylcyclohepta-1,3,5-triene** (**1c**): Colorless crystals, m.p. 43.2–44.5 °C. ¹H NMR (270 MHz, CDCl₃): δ = 1.12 (s, 9 H, *t*Bu), 1.16 (br. s, 9 H, *t*Bu), 1.68 (br. s, 1 H, ≡CH), 3.83 (br. s, 1 H, 7-H), 4.95 (br. d, *J* = 8.2 Hz, 1 H, 6-H), 5.96 (d, *J* = 6.4 Hz, 1 H, 2-H), 6.53 (dd, *J* = 11.0, 6.4 Hz, 1 H, 3-H), 6.65 (dd, *J* = 11.0, 1.3 Hz, 1 H, 4-H) ppm. ¹³C NMR (68 MHz, CDCl₃): δ = 25.1 (br., C-7), 29.2 (br., CH₃), 29.9 (CH₃), 34.8 [br., *C*(CH₃)₃], 35.9 [*C*(CH₃)₃], 65.2 (br., ≡CH), 83.4 (br., *-C*≡CH), 102.5 (br., C-6), 118.3 (C-2), 127.3 (br., C-3), 129.0 (br., C-4), 134.2 (br., C-1 or C-5), 146.3 (br., C-1 or C-5) ppm. IR (KBr): \tilde{v} = 3279 (≡C−H) cm⁻¹. C₁₇H₂₄ (228.37): calcd. C 89.41, H 10.59; found C 89.12, H 10.80.

2,5-Di-*tert*-**butyl-7**-*e***thynylcyclohepta-1,3,5**-*t***riene** (1d): Pale-yellow oil. ¹H NMR (270 MHz, CDCl₃): $\delta = 1.11$ (s, 18 H, *t*Bu), 1.91 (br. s, 1 H, 7-H), 2.11 (d, J = 2.6 Hz, 1 H, ≡CH), 4.37 (br. s, 2 H, 1,6-H), 6.44 (br. s, 2 H, 3,4-H) ppm. ¹³C NMR (68 MHz, CDCl₃, 60 °C): $\delta = 23.6$ (br., C-7), 29.6 (CH₃), 34.7 [*C*(CH₃)₃], 67.8 (≡CH), 86.9 (-C≡CH), 91.5 (br., C-1,6), 125.7 (C-3,4), 144.5 (C-2,5) ppm. IR (neat): $\tilde{\nu} = 3314$ (≡C−H), 2110 (C≡C) cm⁻¹. C₁₇H₂₄ (228.37): calcd. C 89.41, H 10.59; found C 89.51, H 10.60. The ¹H NMR spectroscopic data for 1d are in agreement with previously reported data.^[22]

2,5-Di-tert-butyl-7-cyanocyclohepta-1,3,5-triene (12): A solution of 1,4-di-tert-butyltropylium perchlorate (2.05 g, 6.8 mmol) in CH₃CN (70 mL) was added over a 5 min period to sodium cyanide (1.74 g, 36 mmol) suspended in CH₃CN (200 mL) at -25 °C. The mixture was stirred at -25 °C for 10 min and then for a further 10 min at room temperature. The solution was decanted and the solvents evaporated. The precipitate was dissolved in Et₂O, and the solution was washed with 10% NaCl and dried (MgSO₄) to give a yellow oil (1.64 g). The oil was purified by MPLC (SiO₂, hexane/ Et₂O, 9:1) to afford **12** (0.23 g, 15%) as a colorless oil. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3)$: $\delta = 1.12$ (s, 18 H, *t*Bu), 2.20 (br. s, 1 H, 7-H), 4.44 (br. s, 2 H, 1,6-H), 6.49 (br. s, 2 H, 3,4-H) ppm. ¹³C NMR $(75 \text{ MHz}, \text{ CDCl}_3, 60 \text{ °C})$; $\delta = 20.6 \text{ (br., C-7)}, 29.3 \text{ (CH}_3), 35.0$ [C(CH₃)₃], 86.0 (br., C-1,6), 120.9 (CN), 126.2 (br., C-3,4), 145.4 (C-2,5) ppm. IR (neat): $\tilde{v} = 2240$, 2250 (C=N) cm⁻¹. C₁₆H₂₃N (229.36): calcd. C 83.79, H 10.11; found C 83.71, H 10.20. The ¹H NMR spectroscopic data are in agreement with previously reported data.[29]

2,5-Di-*tert***-butyl-7-vinylcyclohepta-1,3,5-triene (17):** A solution of vinylmagnesium bromide in THF (40 mL) was prepared from vinyl bromide (3.4 g, 32 mmol) and magnesium (0.75 g, 31 mmol). 1,4-Di-*tert*-butyltropylium perchlorate (4.5 g, 15 mmol) was added to this solution at 0 °C, and the temperature was raised to room temperature. Aqueous workup gave a yellow oil (3.7 g), a portion (0.91 g) of which was purified by HPLC (Dupont Zorbax SIL, hexane) to afford **17** (0.22 g, 26%) as a colorless oil. ¹H NMR (270 MHz, CDCl₃): $\delta = 1.10$ (s, 18 H, *t*Bu), 1.53 (m, 1 H, 7-H), 3.94 (br. d, J = 4.3 Hz, 2 H, 1,6-H), 5.02 (d, J = 10.2 Hz, 1 H, = CH₂), 5.09 (d, J = 17.2 Hz, 1 H, =CH₂), 5.93 (m, 1 H, -CH= CH₂), 6.34 (s, 2 H, 3,4-H) ppm. ¹³C NMR (68 MHz, CDCl₃): $\delta = 29.5$ (CH₃), 34.1 (br., C-7), 34.8 [*C*(CH₃)₃], 85.4 (br., C-1,6), 113.2 (=CH₂), 123.8 (br., C-3,4), 141.0 (-CH=CH₂), 144.3 (C-2,5) ppm. HRMS (EI+): calcd. for C₁₇H₂₆ 230.2035 [M⁺]; found 230.2042.

Bis(cyclohepta-2,4,6-trien-1-yl)ethyne (21):^[28] A 1.40 mol·L⁻¹ solution of BuLi in hexane (2.1 mL, 2.9 mmol) was added to **1a** (0.34 g,

2.9 mmol) in dry THF (50 mL) at -68 °C over a 10 min period. Tropylium tetrafluoroborate (0.52 g, 2.9 mmol) was added at -68 °C, and the reaction mixture was stirred at room temperature for 2 h. Water (1 mL) was added, and the THF was evaporated under vacuum. Et₂O and 10% NaCl were added to the residue and the layers separated. The Et₂O layer was dried (MgSO₄) and the solvents were evaporated to give **21** (0.58 g, 97%) as a yellow oil. ¹H NMR (270 MHz, CDCl₃): $\delta = 2.53$ (t, J = 4.6 Hz, 2 H, 7-H), 5.37 (m, 4 H, 1,6-H), 6.17 (m, 4 H, 2,5-H), 6.66 (m, 4 H, 3,4-H) ppm. ¹³C NMR (68 MHz, CDCl₃): $\delta = 31.7$ (C-7), 81.8 (C=C), 123.9 (C-1,6), 124.6 (C-2,5), 131.0 (C-3,4) ppm.

Acid-Catalyzed Rearrangement in THF/TFA. General Procedure: A weighed amount of cycloheptatriene derivative was dissolved in dry THF (5 mL) under argon. TFA (1 mL) was added, and the solution was heated at 60 °C until TLC analysis indicated that all the starting compound had been consumed. The reaction mixture was diluted with Et_2O and washed with 5% NaHCO₃ and with 10% NaCl. The organic layer was dried (MgSO₄) and the solvents were evaporated. The residue was subject to separation and structure analysis.

A. Rearrangement of 1a in THF/TFA: Heating of compound 1a (39.1 mg, 0.384 mmol) in THF/TFA (5:1, v/v) at 60 °C for 40 d gave a yellow oil, the purification of which by HPLC (DuPont Zorbax SIL, hexane) gave 2 (35.8 mg, 92%) as a colorless oil. ¹H NMR (270 MHz, $[D_8]$ THF/TFA, 5:1): $\delta = 5.06$ (d, J = 6.8 Hz, 2 H, = CH₂), 6.12 (t, J = 6.8 Hz, 1 H, -CH=), 7.05-7.33 (m, 5 H, arom. H) ppm. ¹³C NMR (68 MHz, $[D_8]$ THF/TFA, 5:1): $\delta = 78.5$ (= CH₂), 94.3 (-CH=), 127.3 (C-2,6 or C-3,5), 127.5 (C-4), 129.2 (C-2,6 or C-3,5), 134.9 (C-1), 210.5 (=C=) ppm. These spectroscopic data are in agreement with previously reported data.^[30,31]

B. Rearrangement of 1b in THF/TFA: Heating compound 1b (34.5 mg) in THF/TFA (5:1, v/v) at 60 °C for 24 h gave a yellow oil, which was shown to be a mixture of **3** and **6** (68:32 molar ratio) by ¹H NMR spectroscopy. The mixture was separated by GPC to afford **3** (18.7 mg, 54%) and **6** (6.0 mg, 18%) in pure forms.

1,4-Di-*tert***-butyl-2-(1,2-propadienyl)benzene (3):** Colorless oil. ¹H NMR (270 MHz, CDCl₃): $\delta = 1.31$ (s, 9 H, *t*Bu), 1.43 (s, 9 H, *t*Bu), 5.09 (d, J = 6.8 Hz, 2 H, =CH₂), 6.81 (t, J = 6.8 Hz, 1 H, -CH=), 7.17 (dd, J = 8.6, 2.3 Hz, 1 H, 5-H), 7.31 (d, J = 8.6 Hz, 1 H, 6-H), 7.50 (d, J = 2.3 Hz, 1 H, 3-H) ppm. ¹³C NMR (68 MHz, CDCl₃): $\delta = 31.2$ (CH₃), 31.4 (CH₃), 34.2 [*C*(CH₃)₃], 35.0 [*C*(CH₃)₃], 77.5 (=CH₂), 94.4 (-CH=), 123.9 (C-5), 125.8 (C-6), 126.9 (C-3), 131.2 (C-2), 143.6 (C-1 or C-4), 148.5 (C-1 or C-4), 209.5 (=C=) ppm. IR (neat): $\tilde{v} = 1942$ (C=C=C) cm⁻¹. HRMS (FAB+): calcd. for C₁₇H₂₄ 228.1878 [M⁺]; found 228.1875.

1-*tert*-**Butyl-4-(1,2-propadienyl)benzene (6):** Colorless oil. ¹H NMR (400 MHz, CDCl₃): $\delta = 1.31$ (s, 9 H, *t*Bu), 5.12 (d, J = 6.8 Hz, 2 H, =CH₂), 6.15 (t, J = 6.8 Hz, 1 H, -CH=), 7.23 (d, J = 8.6 Hz, 2 H, 2,6-H or 3,5-H), 7.33 (d, J = 8.6 Hz, 2 H, 2,6-H or 3,5-H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 31.3$ (CH₃), 34.5 [*C*(CH₃)₃], 78.6 (=CH₂), 93.6 (-CH=), 125.6 (C-2,6 or -C-3,5), 126.4 (C-2,6 or C-3,5), 130.9 (C-4), 150.0 (C-1), 209.8 (=C=) ppm. IR (neat): $\tilde{v} = 1942$ (C=C=C) cm⁻¹. The NMR spectroscopic data are in agreement with previously reported data.^[32]

C. Rearrangement of 1c in THF/TFA: Heating of compound 1c (31.5 mg) in THF/TFA (5:1, v/v) at 60 °C for 24 h gave a yellow oil, which was shown to be a mixture of 7 and 8 (93.4:6.6 molar ratio) by ¹H NMR spectroscopy. The mixture was separated by GPC to afford 7 (28.0 mg, 89%) and 8 (2.0 mg, 6%).

1,3-Di-*tert*-butyl-2-(1,2-propadienyl)benzene (7): Colorless oil. ¹H NMR (270 MHz, CDCl₃): $\delta = 1.45$ (s, 18 H, *t*Bu), 4.69 (d, J = 6.9 Hz, 2 H, =CH₂), 6.53 (t, J = 6.9 Hz, 1 H, -CH=), 7.16 (t, J = 7.9 Hz, 1 H, 5-H), 7.35 (d, J = 7.9 Hz, 2 H, 4,6-H) ppm. ¹³C NMR (68 MHz, CDCl₃): $\delta = 31.8$ (CH₃), 36.8 [*C*(CH₃)₃], 74.8 (= CH₂), 94.7 (-CH=), 124.4 (C-4,6), 126.7 (C-5), 132.8 (C-2), 149.5 (C-1,3), 208.4 (=C=) ppm. IR (neat): $\tilde{v} = 1959$ (C=C=C) cm⁻¹. HRMS (FAB+): calcd. for C₁₇H₂₄ 228.1878 [M⁺]; found 228.1884.

1-*tert*-**Butyl-3**-(**1**,**2**-**propadienyl)benzene (8):** Colorless oil. ¹H NMR (270 MHz, CDCl₃): $\delta = 1.32$ (s, 9 H, *t*Bu), 5.14 (d, J = 6.6 Hz, 2 H, =CH₂), 6.17 (t, J = 6.6 Hz, 1 H, -CH=), 7.09-7.37 (m, 4 H, arom. H) ppm. ¹³C NMR (68 MHz, CDCl₃): $\delta = 31.3$ (CH₃), 34.7 [*C*(CH₃)₃], 78.7 (=CH₂), 94.3 (-CH=), 123.7, 123.9, 124.0, 128.3 (arom. CH), 133.4, 151.5, 209.8 (arom. C) ppm. IR (neat): $\tilde{\nu} = 1943$ (C=C=C) cm⁻¹. HRMS (FAB+): calcd. for C₁₃H₁₆ 172.1252 [M⁺]; found 172.1253.

D. Rearrangement of 1d in THF/TFA: Heating of compound 1d (44.0 mg) in THF/TFA (5:1, v/v) at 60 °C for 3 h gave a yellow oil, which was shown to be essentially pure 3 by ¹H NMR spectroscopy. Purification by HPLC (DuPont Zorbax SIL, hexane) gave 3 (41.6 mg, 95%), which showed ¹H and ¹³C NMR spectra identical to those of 3 obtained by the rearrangement of 1b.

E. Rearrangement of 17 in THF/TFA: Heating of compound **17** (90.0 mg) in THF/TFA (5:1, v/v) at 60 °C for 29 h gave a yellow oil, which was shown to be a mixture of (*E*)-**20** and (*Z*)-**20** (66:34 molar ratio) by ¹H NMR spectroscopy. The mixture was separated by HPLC (DuPont Zorbax SIL, hexane) to afford (*E*)-**20** (41.8 mg, 46%) and (*Z*)-**20** (21.3 mg, 24%).

(*E*)-1,4-Di-*tert*-butyl-2-(1-propenyl)benzene [(*E*)-20]: Colorless oil. ¹H NMR (270 MHz, CDCl₃): $\delta = 1.32$ (s, 9 H, *t*Bu), 1.40 (s, 9 H, *t*Bu), 1.90 (dd, J = 6.6, 2.0 Hz, 3 H, =CHCH₃), 5.85 (dq, J = 15.2, 6.6 Hz, 1 H, =CHCH₃), 7.01 (dd, J = 15.2, 2.0 Hz, 1 H, -CH=CHCH₃), 7.18 (dd, J = 8.3, 2.4 Hz, 1 H, 5-H), 7.28 (d, J = 8.3 Hz, 1 H, 6-H), 7.32 (d, J = 2.4 Hz, 1 H, 3-H) ppm. ¹³C NMR (68 MHz, CDCl₃): $\delta = 18.8$ (=CHCH₃), 31.30 [C(CH₃)₃], 31.32 [C(CH₃)₃], 34.2 [C(CH₃)₃], 35.3 [C(CH₃)₃], 123.6 (C-5), 125.3 (C-6), 126.1 (=CHCH₃), 126.5 (C-3), 133.7 (-CH=CHCH₃), 137.6, 143.7, 148.4 (arom. C) ppm. C₁₇H₂₆ (230.39): calcd. C 88.63, H 11.37; found C 88.46, H 11.64.

(*Z*)-1,4-Di-*tert*-butyl-2-(1-propenyl)benzene [(*Z*)-20]: Colorless oil. ¹H NMR (270 MHz, CDCl₃): $\delta = 1.30$ (s, 9 H, *t*Bu), 1.36 (s, 9 H, *t*Bu), 1.63 (dd, *J* = 6.9, 1.8 Hz, 3 H, =CHCH₃), 5.74 (dq, *J* = 11.2, 6.9 Hz, 1 H, =CHCH₃), 6.86 (dd, *J* = 11.2, 1.8 Hz, 1 H, -CH=CHCH₃), 7.09 (d, *J* = 2.2 Hz, 1 H, 3-H), 7.20 (dd, *J* = 8.2, 2.2 Hz, 1 H, 5-H), 7.33 (d, *J* = 8.2 Hz, 1 H, 6-H) ppm. ¹³C NMR (68 MHz, CDCl₃): $\delta = 14.3$ (=CHCH₃), 30.6 [C(CH₃)₃], 31.3 [C(CH₃)₃], 34.1 [C(CH₃)₃], 35.4 [C(CH₃)₃], 123.2 (C-5), 125.0 (= CHCH₃), 125.4 (C-6), 129.3 (C-3), 133.9 (-*C*H=CHCH₃), 136.2, 145.1, 147.8 (arom. C) ppm. HRMS (EI+): calcd. for C₁₇H₂₆ 230.2035[M⁺]; found 230.2038.

Kinetic Measurements of the Acid-Catalyzed Rearrangements of 1a-d: A solution of a starting compound (0.02-0.57 mmol) in a mixture of [D₈]THF (0.7 mL) and TFA (0.14 mL) was placed in an NMR sample tube. The tube was filled with argon, sealed, and heated in a thermostatted oil bath at 60 °C. The reaction was monitored by the integrations of the following ¹H NMR peaks. 1a, 1,4-H; 1b, 6-H; 1c, 2-H; 1d, 1,6-H; 2, =CH₂; 3, =CH₂ and -CH=; 6, =CH₂; 7, =CH₂; 8, -CH=. The reaction followed first-order kinetics over three half lives.

FULL PAPER

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- ^[1] T. Steiner, M. Tamm, J. Organomet. Chem. **1998**, 570, 235–239.
- ^[2] M. Tamm, T. Jentzsch, W. Werncke, Organometallics 1997, 16, 1418-1424.
- ^[3] T. Kitagawa, J. Kamada, S. Minegishi, K. Takeuchi, Org. Lett. 2000, 2, 3011–3013.
- [4] A. A. Jarzecki, J. Gajewski, E. R. Davidson, J. Am. Chem. Soc. 1999, 121, 6928-6935.
- [5] G. A. Olah, A. Molnár, *Hydrocarbon Chemistry*, Wiley-Interscience, New York, **1995**, pp. 120–122.
- [6] P. D. Landor, In *The Chemistry of the Allenes* (Ed.: S. R. Landor), Academic Press, London, **1982**, vol. 1, chapter 2.
- [7] The Chemistry of Ketenes, Allenes, and Related Compounds (Ed.: S. Patai), John Wiley & Sons, Chichester, 1980, part 2, chapters 15 and 20.
- ^[8] C. A. Buehler, D. E. Pearson, *Survey of Organic Syntheses*, Wiley-Interscience, New York, **1970**, vol. 1, chapter 3.
- ^[9] D. R. Taylor, Chem. Rev. 1967, 67, 317-358.
- ^[10] B. J. Barry, W. J. Beale, M. D. Carr, S.-K. Hei, I. Reid, J. Chem. Soc., Chem. Commun. 1973, 177.
- ^[11] M. Balci, Turkish J. Chem. 1992, 16, 42-90.
- ^[12] G. Maier, Angew. Chem. Int. Ed. Engl. 1967, 6, 402-413.
- ^[13] E. Vogel, Pure Appl. Chem. 1969, 20, 237-262.
- [14] A review of the trapping of vinyl cation intermediates under solvolytic conditions: T. Kitamura, H. Taniguchi, Y. Tsuno, in *Dicoordinated Carbocations* (Eds.: Z. Rappoport, P. J. Stang), John Wiley & Sons, Chichester, **1997**, chapter 7, pp. 321–376.
- ^[15] K. Takeuchi, H. Fujimoto, T. Kitagawa, H. Fujii, K. Okamoto, J. Chem. Soc., Perkin Trans. 2 1984, 461–467.
- ^[16] K. Takeuchi, H. Fujimoto, K. Okamoto, *Tetrahedron Lett.* 1981, 22, 4981–4984.
- [¹⁷] [^{17a]} E. Ciganek, J. Am. Chem. Soc. **1965**, 87, 1149–1150. [^{17b]}
 E. Ciganek, J. Am. Chem. Soc. **1967**, 89, 1454–1458. [^{17c]}
 E. Ciganek, J. Am. Chem. Soc. **1971**, 93, 2207–2215.
- ^[18] The absence of the (E,E), (E,Z), and (Z,Z) isomers of 1,4-diphenyl-1,3-butadiene was confirmed by comparing the ¹H NMR spectrum of the reaction mixture with those reported:

^[18a] S.-K. Kang, J.-S. Kim, S.-C. Choi, J. Org. Chem. **1997**, 62, 4208–4209. ^[18b] C. Cannes, S. Condon, M. Durandetti, J. Périchon, J.-Y. Nédélec, J. Org. Chem. **2000**, 65, 4575–4583.

- ^[19] K. Takeuchi, T. Kitagawa, A. Ueda, Y. Senzaki, K. Okamoto, *Tetrahedron* **1985**, *41*, 5455-5463.
- ^[20] K. Takeuchi, T. Kitagawa, T. Toyama, K. Okamoto, J. Chem. Soc., Chem. Commun. 1982, 313–314.
- ^[21] K. Takeuchi, M. Arima, K. Okamoto, *Tetrahedron Lett.* 1981, 22, 3081–3084.
- [22] K. Takeuchi, Y. Senzaki, K. Okamoto, J. Chem. Soc., Chem. Commun. 1984, 111–112.
- [23] D. Cremer, B. Dick, Angew. Chem. Int. Ed. Engl. 1982, 21, 865–866.
- ^[24] K. Conrow, Org. Synth. Coll. Vol. 1973, 5, 1138-1140.
- ^[25] K. Komatsu, K. Takeuchi, M. Arima, Y. Waki, S. Shirai, K. Okamoto, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3257–3261.
- ^[26] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian 98, Revision A.9, Gaussian, Inc., Pittsburgh PA, 1998.
- ^[27] M. M. Midland, J. I. McLoughlin, R. T. Werley, Jr., Org. Synth. Coll. Vol. **1993**, 8, 391–396.
- ^[28] R. M. Hoskinson, Aust. J. Chem. 1970, 23, 399-402.
- ^[29] K. Takeuchi, T. Kitagawa, Y. Senzaki, H. Fujimoto, K. Okamoto, *Chem. Lett.* **1983**, 69–72.
- ^[30] A. Maercker, J. Fischenich, *Tetrahedron* **1995**, *51*, 10209–10218.
- [^{31]} T. Okuyama, K. Izawa, T. Fueno, J. Am. Chem. Soc. 1973, 95, 6749-6752.
- ^[32] E. Fouquet, M. Pereyre, A. L. Rodriguez, J. Org. Chem. 1997, 62, 5242-5243.

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