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

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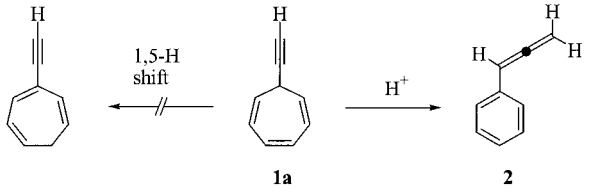
The acid-catalyzed rearrangement in THF/TFA (5:1, v/v) of cyclohepta-1,3,5-trienes containing an α,β-unsaturated substituent at C-7 was investigated. 7-Ethynylcyclohepta-1,3,5-triene (**1a**) and its 1,4-di-*tert*-butyl (**1b**), 1,5-di-*tert*-butyl (**1c**), and 2,5-di-*tert*-butyl (**1d**) derivatives 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 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 ^{13}C NMR chemical shifts of **1a**–**d**, indicating the importance of the equilibrium concentration of the norcaradiene form as a rate-controlling factor.

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 thermal 1,5-hydrogen shift, a reaction which is normally observed for cyclohepta-1,3,5-trienes at temperatures higher than 100 °C.[4]



Scheme 1

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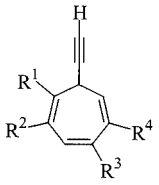
(Table 1). The rearrangement of **1a** and **1d** gave phenylallenes **2** and **3**, respectively, as the sole products. A plausible pathway, shown in Scheme 2, includes an initial cycloheptatriene (CHT)−norcaradiene (NCD) equilibrium.[11−13] The three-membered ring of the protonated form of the NCD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

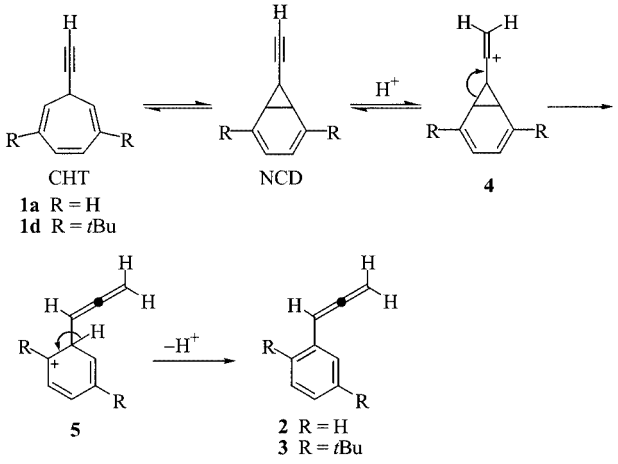


	R^1	R^2	R^3	R^4
1a	H	H	H	H
1b	*t*Bu	H	*t*Bu	H
1c	*t*Bu	H	H	*t*Bu
1d	H	*t*Bu	H	*t*Bu

Table 1. TFA-catalyzed rearrangement of 7-ethynylcyclohepta-1,3,5-trienes **1a**−**d**[a]

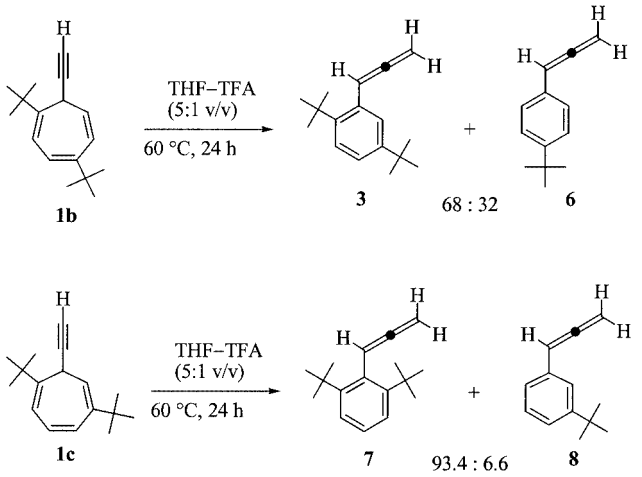
	Substituents on sp^2 C atoms	Time [h][b]	Product
1a	none	960	**2**
1b	1,4-(*t*Bu)$_2$	24	**3** + **6** (68:32)
1c	1,5-(*t*Bu)$_2$	24	**7** + **8** (93.4:6.6)
1d	2,5-(*t*Bu)$_2$	3	**3**

[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.



Scheme 2

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



Scheme 3

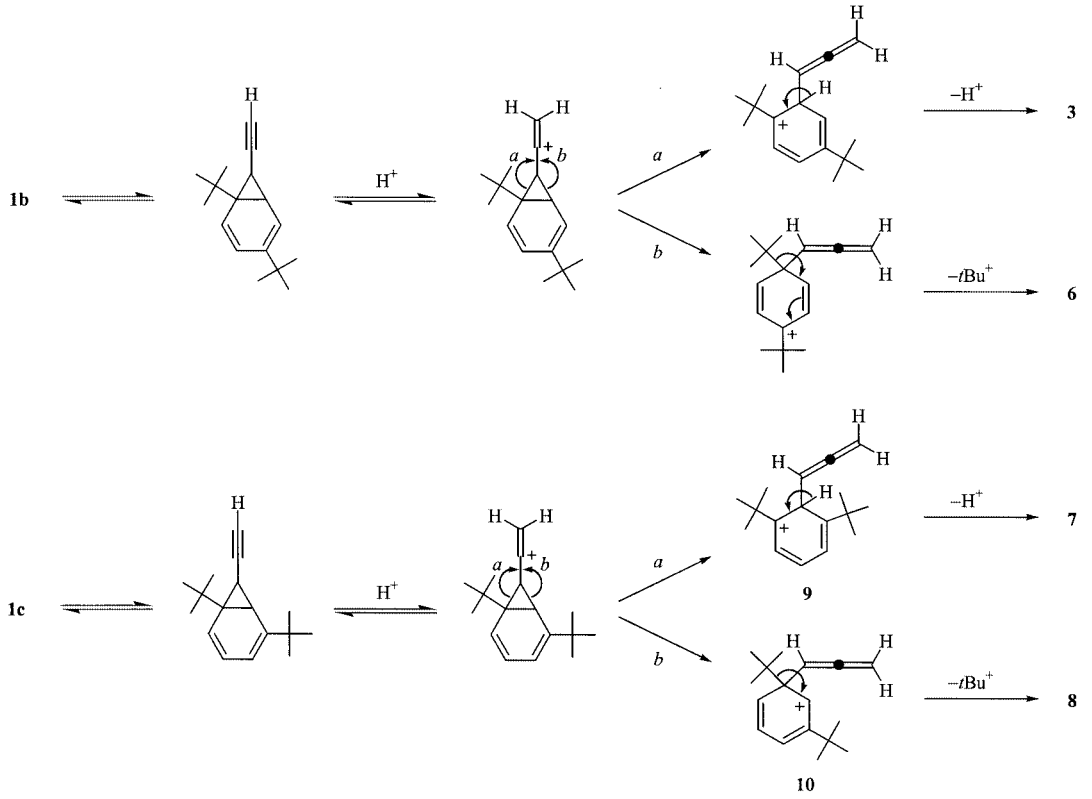
contrast, the pentadienyl cation moiety of **10** contains only one *tert*-butyl group at C-2, where the distribution of the positive charge should be small.

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 M 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 allenyl 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

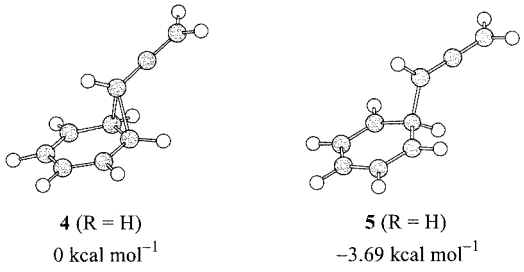
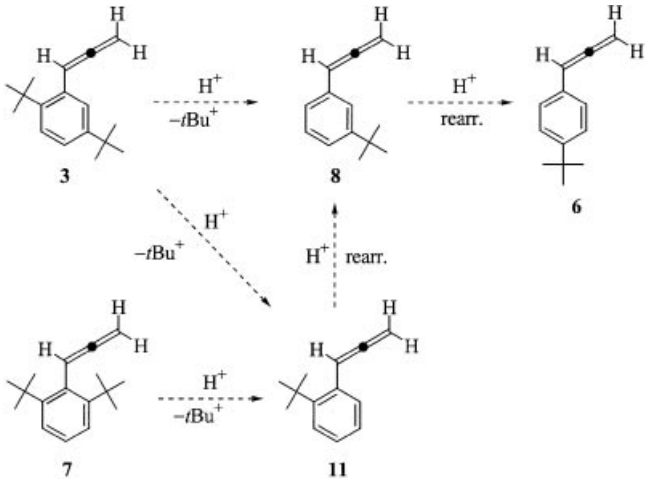
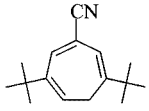


Figure 1. Optimized structures and relative energies of the intermediate cations **4** (R = H) and **5** (R = H) obtained by the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level of theory



Scheme 5

(Scheme 6). This transformation may be more favorable than the rearrangement of 7-ethynyl derivatives, because an 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 ^{1}H NMR spectrum of the reaction mixture showed signals at δ = 2.23 (d, J = 8.0 Hz) and δ = 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** ⟷**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 kcal·mol^{-1}.



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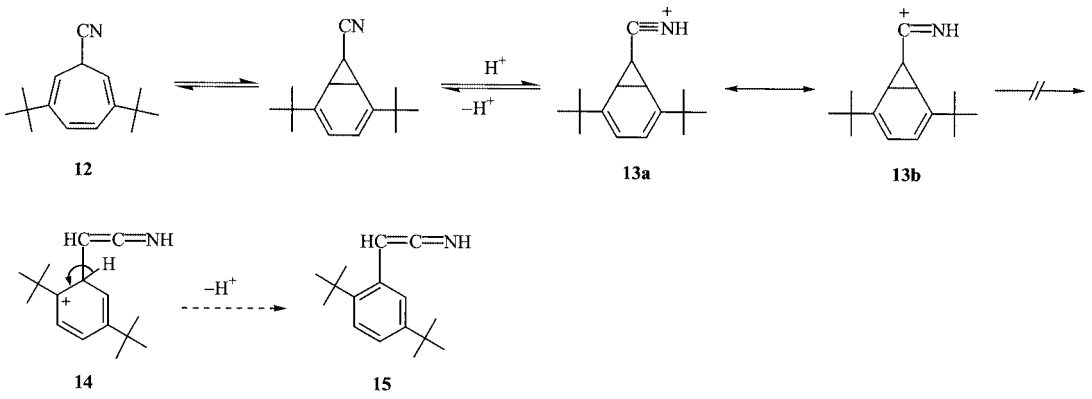
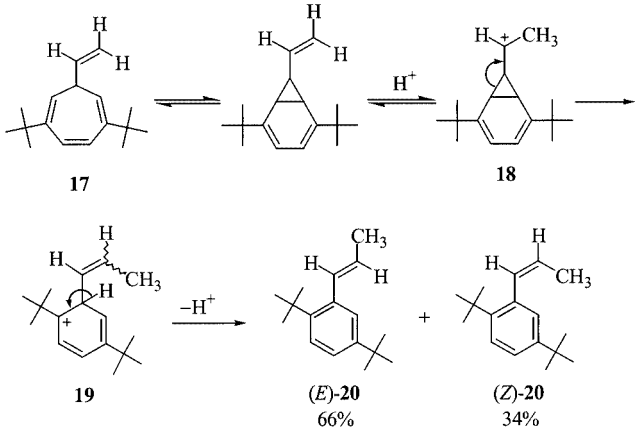
On the other hand, 7-vinylcyclohepta-1,3,5-triene **17** cleanly rearranged in THF/TFA (5:1, v/v) at 60 °C to give (1-propenyl)benzenes (*E*)-**20** and (*Z*)-**20**, which were separable



Scheme 6

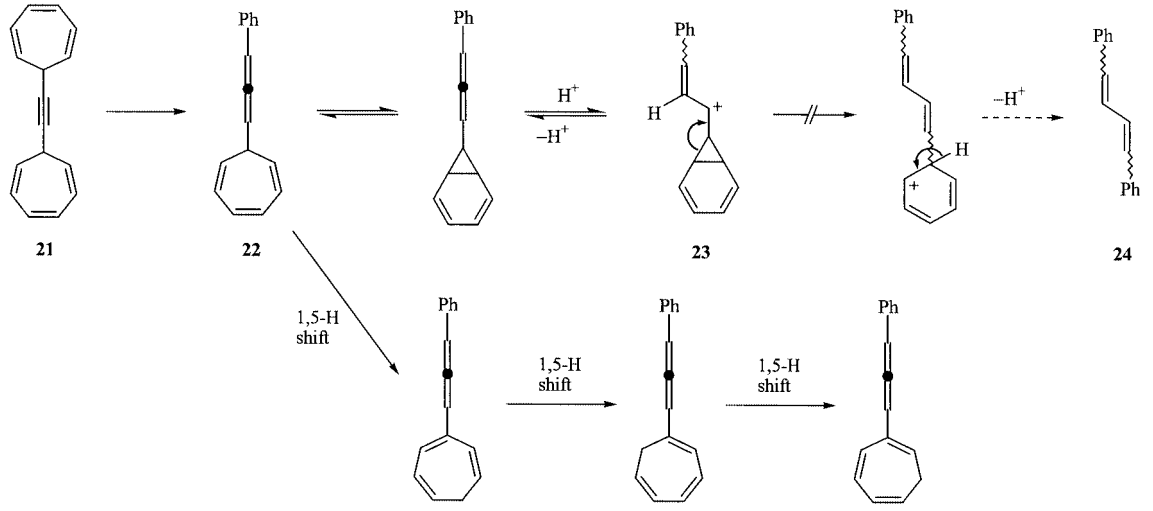


Scheme 7

by HPLC (SiO_2), 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**.

Acid-Catalyzed Rearrangement of Bis(cyclohepta-2,4,6-trien-1-yl)ethyne

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 acid-catalyzed 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 [D_8]THF/TFA (5:1, v/v) by using an NMR sample tube. The progress of the reaction was monitored by integration of the ^{1}H NMR peaks. The decay of the starting compounds followed the first-order kinetics. The obtained rate constants are listed in Table 2.

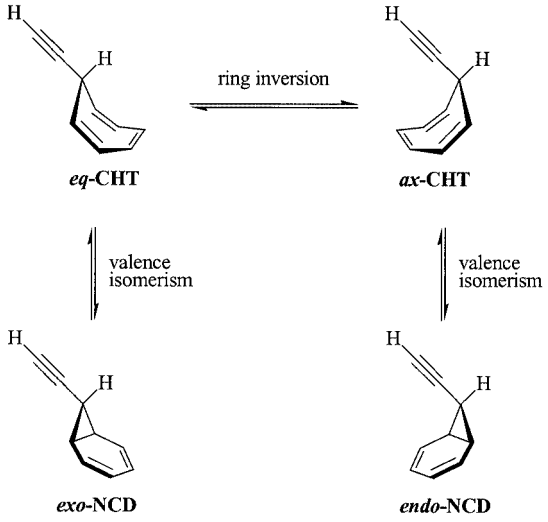
Table 2. Rate constants (k_1) for acid-catalyzed rearrangement, ^{13}C chemical shifts (δ), and calculated energy of the conformers/isomers of **1a**−**d**

	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 (*ax*-CHT) 0.00 (*eq*-CHT) 6.62 (*endo*-NCD) 4.65 (*exo*-NCD)
1b	28.6	117.7	0.00 (*ax*-CHT) 0.81 (*eq*-CHT) 4.13 (*endo*-NCD) 5.13 (*exo*-NCD)
1c	46.8	102.5	0.00 (*ax*-CHT) 0.41 (*eq*-CHT) 3.79 (*endo*-NCD) 4.57 (*exo*-NCD)
1d	322	91.5	3.47 (*ax*-CHT) 0.00 (*eq*-CHT) 3.44 (*endo*-NCD) 1.17 (*exo*-NCD)

[a] In [D_8]THF/TFA (5:1, v/v), at 60 °C. [b] In $CDCl_3$, 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-1,3,5-triene by the HF/6-31G(d) level.[23] The CHT−NCD energy gap (kcal·mol^{-1}) decreased in the order **1a** (4.65) > **1b** (4.13) > **1c** (3.79) > **1d** (1.17).



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

The increase in the fraction of the norcaradiene form can be also estimated by the ^{13}C 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 sp^2 to sp^3 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 *t*Bu) is negligible, the observed C-6 chemical shifts δ(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-1,3,5-trienes were found to undergo clean rearrangement to form phenylallene and (1-propenyl)benzene derivatives respectively, under acidic conditions. The rearrangement of 7-ethynylcyclohepta-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 1,5-hydrogen 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 three-membered ring of the norcaradiene structure should be energetically favorable for a clean acid-catalyzed rearrange-

ment 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: ^{1}H and ^{13}C NMR spectra were obtained with JEOL-EX400 (^{1}H, 400 MHz; ^{13}C, 100 MHz), AL300 (^{1}H, 300 MHz; ^{13}C, 75 MHz), and GSX270 (^{1}H, 270 MHz; ^{13}C, 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 1,4-di-*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. ^{1}H NMR (400 MHz, $CDCl_3$): 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. ^{13}C NMR (68 MHz, $CDCl_3$): 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): $\tilde{\nu}$ = 3303 (≡C−H), 2126 (C≡C) cm^{-1}. The ^{1}H 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 (SiO_2, 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. ^{1}H NMR (270 MHz, $CDCl_3$): 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. ^{13}C NMR (68 MHz, $CDCl_3$, 60 °C): δ = 29.0 (C-7), 29.7 (CH_3), 30.2 (CH_3), 35.6 [*C*(CH_3)$_3$], 36.2 [*C*(CH_3)$_3$], 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): $\tilde{\nu}$ = 3278 (≡C−H) cm^{-1}. $C_{17}H_{24}$ (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. ^{1}H NMR (270 MHz, $CDCl_3$): 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. ^{13}C NMR (68 MHz, $CDCl_3$): δ = 25.1 (br., C-7), 29.2 (br., CH_3), 29.9 (CH_3), 34.8 [br., *C*(CH_3)$_3$], 35.9 [*C*(CH_3)$_3$], 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): $\tilde{\nu}$ = 3279 (≡C−H) cm^{-1}. $C_{17}H_{24}$ (228.37): calcd. C 89.41, H 10.59; found C 89.12, H 10.80.

2,5-Di-*tert*-butyl-7-ethynylcyclohepta-1,3,5-triene (1d): Pale-yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 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. ^{13}C NMR (68 MHz, $CDCl_3$, 60 °C): δ = 23.6 (br., C-7), 29.6 (CH_3), 34.7 [*C*(CH_3)$_3$], 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}. $C_{17}H_{24}$ (228.37): calcd. C 89.41, H 10.59; found C 89.51, H 10.60. The ^{1}H 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 CH_3CN (70 mL) was added over a 5 min period to sodium cyanide (1.74 g, 36 mmol) suspended in CH_3CN (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 Et_2O, and the solution was washed with 10% NaCl and dried ($MgSO_4$) to give a yellow oil (1.64 g). The oil was purified by MPLC (SiO_2, hexane/Et_2O, 9:1) to afford **12** (0.23 g, 15%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 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. ^{13}C NMR (75 MHz, $CDCl_3$, 60 °C): δ = 20.6 (br., C-7), 29.3 (CH_3), 35.0 [*C*(CH_3)$_3$], 86.0 (br., C-1,6), 120.9 (CN), 126.2 (br., C-3,4), 145.4 (C-2,5) ppm. IR (neat): $\tilde{\nu}$ = 2240, 2250 (C≡N) cm^{-1}. $C_{16}H_{23}N$ (229.36): calcd. C 83.79, H 10.11; found C 83.71, H 10.20. The ^{1}H 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. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 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, =CH_2), 5.09 (d, *J* = 17.2 Hz, 1 H, =CH_2), 5.93 (m, 1 H, −C*H*=CH_2), 6.34 (s, 2 H, 3,4-H) ppm. ^{13}C NMR (68 MHz, $CDCl_3$): δ = 29.5 (CH_3), 34.1 (br., C-7), 34.8 [*C*(CH_3)$_3$], 85.4 (br., C-1,6), 113.2 (=CH_2), 123.8 (br., C-3,4), 141.0 (−*C*H=CH_2), 144.3 (C-2,5) ppm. HRMS (EI+): calcd. for $C_{17}H_{26}$ 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. Et_2O and 10% NaCl were added to the residue and the layers separated. The Et_2O layer was dried ($MgSO_4$) and the solvents were evaporated to give **21** (0.58 g, 97%) as a yellow oil. ^1H NMR (270 MHz, $CDCl_3$): δ = 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. ^{13}C NMR (68 MHz, $CDCl_3$): δ = 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% $NaHCO_3$ and with 10% NaCl. The organic layer was dried ($MgSO_4$) 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): δ = 5.06 (d, *J* = 6.8 Hz, 2 H, =CH_2), 6.12 (t, *J* = 6.8 Hz, 1 H, −CH=), 7.05−7.33 (m, 5 H, arom. H) ppm. ^{13}C NMR (68 MHz, [D_8]THF/TFA, 5:1): δ = 78.5 (=CH_2), 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, $CDCl_3$): δ = 1.31 (s, 9 H, *t*Bu), 1.43 (s, 9 H, *t*Bu), 5.09 (d, *J* = 6.8 Hz, 2 H, =CH_2), 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. ^{13}C NMR (68 MHz, $CDCl_3$): δ = 31.2 (CH_3), 31.4 (CH_3), 34.2 [*C*(CH_3)$_3$], 35.0 [*C*(CH_3)$_3$], 77.5 (=CH_2), 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): $\tilde{\nu}$ = 1942 (C=C=C) cm^{-1}. HRMS (FAB+): calcd. for $C_{17}H_{24}$ 228.1878 [M^+]; found 228.1875.

1-*tert*-Butyl-4-(1,2-propadienyl)benzene (6): Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 9 H, *t*Bu), 5.12 (d, *J* = 6.8 Hz, 2 H, =CH_2), 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. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.3 (CH_3), 34.5 [*C*(CH_3)$_3$], 78.6 (=CH_2), 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): $\tilde{\nu}$ = 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, $CDCl_3$): δ = 1.45 (s, 18 H, *t*Bu), 4.69 (d, *J* = 6.9 Hz, 2 H, =CH_2), 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. ^{13}C NMR (68 MHz, $CDCl_3$): δ = 31.8 (CH_3), 36.8 [*C*(CH_3)$_3$], 74.8 (=CH_2), 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): $\tilde{\nu}$ = 1959 (C=C=C) cm^{-1}. HRMS (FAB+): calcd. for $C_{17}H_{24}$ 228.1878 [M^+]; found 228.1884.

1-*tert*-Butyl-3-(1,2-propadienyl)benzene (8): Colorless oil. ^1H NMR (270 MHz, $CDCl_3$): δ = 1.32 (s, 9 H, *t*Bu), 5.14 (d, *J* = 6.6 Hz, 2 H, =CH_2), 6.17 (t, *J* = 6.6 Hz, 1 H, −CH=), 7.09−7.37 (m, 4 H, arom. H) ppm. ^{13}C NMR (68 MHz, $CDCl_3$): δ = 31.3 (CH_3), 34.7 [*C*(CH_3)$_3$], 78.7 (=CH_2), 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 $C_{13}H_{16}$ 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 ^{13}C 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, $CDCl_3$): δ = 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, =CHC*H*$_3$), 5.85 (dq, *J* = 15.2, 6.6 Hz, 1 H, =C*H*CH$_3$), 7.01 (dd, *J* = 15.2, 2.0 Hz, 1 H, −C*H*=CHCH$_3$), 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. ^{13}C NMR (68 MHz, $CDCl_3$): δ = 18.8 (=CH*C*H$_3$), 31.30 [C(*C*H$_3$)$_3$], 31.32 [C(*C*H$_3$)$_3$], 34.2 [*C*(CH$_3$)$_3$], 35.3 [*C*(CH$_3$)$_3$], 123.6 (C-5), 125.3 (C-6), 126.1 (=*C*HCH$_3$), 126.5 (C-3), 133.7 (−*C*H=CHCH$_3$), 137.6, 143.7, 148.4 (arom. C) ppm. $C_{17}H_{26}$ (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, $CDCl_3$): δ = 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, =CHC*H*$_3$), 5.74 (dq, *J* = 11.2, 6.9 Hz, 1 H, =C*H*CH$_3$), 6.86 (dd, *J* = 11.2, 1.8 Hz, 1 H, −C*H*=CHCH$_3$), 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. ^{13}C NMR (68 MHz, $CDCl_3$): δ = 14.3 (=CH*C*H$_3$), 30.6 [C(*C*H$_3$)$_3$], 31.3 [C(*C*H$_3$)$_3$], 34.1 [*C*(CH$_3$)$_3$], 35.4 [*C*(CH$_3$)$_3$], 123.2 (C-5), 125.0 (=*C*HCH$_3$), 125.4 (C-6), 129.3 (C-3), 133.9 (−*C*H=CHCH$_3$), 136.2, 145.1, 147.8 (arom. C) ppm. HRMS (EI+): calcd. for $C_{17}H_{26}$ 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 [D_8]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**, =CH_2; **3**, =CH_2 and −CH=; **6**, =CH_2; **7**, =CH_2; **8**, −CH=. The reaction followed first-order kinetics over three half lives.

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