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Acid-Catalyzed Rearrangement of Ethynylcycloheptatriene to Phenylallene

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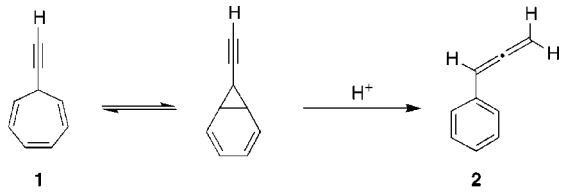
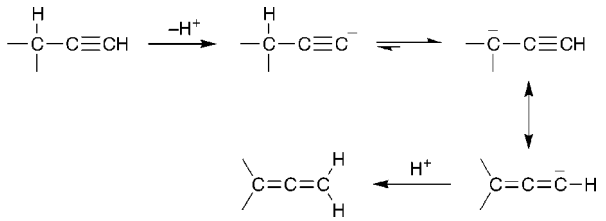
ABSTRACT



7-Ethynylcycloheptatriene (1) cleanly isomerizes to phenylallene in the presence of acid. A mechanism involving the protonation of ethynylnorcaradiene, which is in equilibrium with 1, followed by the cleavage of a three-membered ring to give an arenium ion, is proposed. The rearrangement is accelerated by a factor of 370 by introducing *tert*-butyl groups on C-2 and C-5, indicating the importance of the equilibrium concentration of the norcaradiene form as a rate-controlling factor.

The acetylene-allene rearrangement[1] is an important method for the synthesis of allenes, since acetylenes which contain a variety of substituents are readily available. This reaction, formally a 1,3-hydrogen shift, is subject to both acid and base catalysis. However, most of the synthetic and mechanistic studies have been performed under basic conditions (Scheme 1), and only a few examples of isomerization in acidic media have been reported.[2] One of the practical disadvantages of the acetylene−allene rearrangement is its reversibility, the result of which is that the product is often a mixture of the desired allene and isomeric acetylenes. One would expect that, if the formation of an allenyl group is accompanied by a concomitant skeletal rearrangement to form a resonance-stabilized carbocation, the reaction would become irreversible, giving an allene in a high yield under relatively mild conditions. We now report the clean transformation of 7-ethynylcycloheptatriene and its derivative into arylallenes via an arenium ion in the presence of acid.

Scheme 1



When heated at 60 °C in a solution of THF containing 2.2 M (17 vol %) of trifluoroacetic acid (TFA), 7-ethynylcycloheptatriene **1**[3] isomerized to phenylallene **2** with a half-life of 9 days. After 50 days, **2** was obtained in nearly quantitative yield.[4] The isomerization was much faster in methanol containing 0.5 M HCl, wherein the reaction was complete in 9 h at 60 °C.

(1) (a) Olah, G. A.; Molnár, Á. *Hydrocarbon Chemistry*; Wiley-Interscience: New York, 1995; pp 120−122. (b) Landor, P. D. In *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic Press: London, 1982; Vol. 1, Chapter 2. (c) *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S., Ed.; John Wiley & Sons: Chichester, 1980; Part 2, Chapters 15 and 20. (d) Buehler C. A.; Pearson D. E. *Survey of Organic Syntheses*; Wiley-Interscience: New York, 1970; Vol. 1, Chapter 3. (e) Taylor, D. R. *Chem. Rev.* **1967**, *67*, 317.

(2) Barry, B. J.; Beale, W. J.; Carr, M. D.; Hei, S.-K.; Reid, I. *J. Chem. Soc., Chem. Commun.* **1973**, 177.

(3) 7-Ethynylcycloheptatriene **1** was synthesized in 68% yield by the reaction of tropylium tetrafluoroborate with 0.97 equiv of ethynyllithium in THF at −78 °C. A byproduct, 1,2-bis(2,4,6-cycloheptatrien-1-yl)ethyne was separated by MPLC and obtained in 5.6% yield. The ^{1}H NMR spectra of both products were identical with those published: Hoskinson, R. M. *Aust. J. Chem.* **1970**, *23*, 399.

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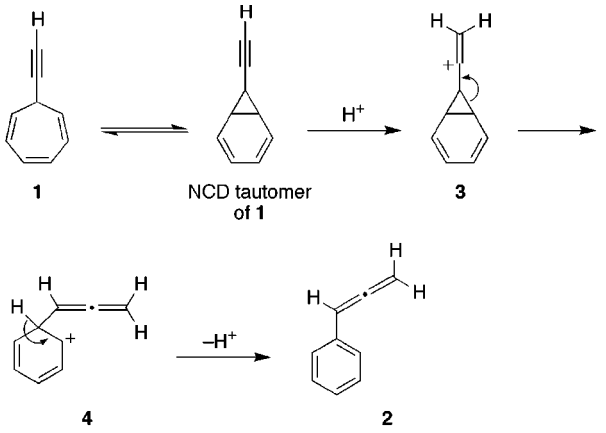
Scheme 2 shows a plausible pathway for the formation of phenylallene. Cycloheptatriene **1** initially undergoes valence

Scheme 2



tautomerism to the norcaradiene form, the protonation of the terminal sp carbon of which generates a vinyl cation **3**. Subsequent cleavage of the three-membered ring forms an arenium ion containing an allenyl group, **4**, which, on deprotonation, readily affords the final product.

In general, thermal equilibrium between a cycloheptatriene (CHT) and its norcaradiene tautomer (NCD) lies heavily in favor of the CHT form. HF/6-31G* calculations have shown that the difference in free energies between the parent CHT and NCD is 5.6 kcal mol^{-1}.[5] Although the π-acceptor ability of the ethynyl group attached at C-7 is expected to shift the equilibrium to some extent toward the NCD side, the concentration of the NCD tautomer at equilibrium is still too low to be detected by NMR. We have reported that the introduction of bulky substituents to the olefinic carbon of the cycloheptatriene ring raises the energy level of the CHT form.[6,7] Thus, 2,5-di-*tert*-butyl-7-ethynylcycloheptatriene **5** is known to exist as a mixture of valence (and conformational) isomers, the populations of which have been determined by low-temperature NMR measurements (Figure 1).[7]

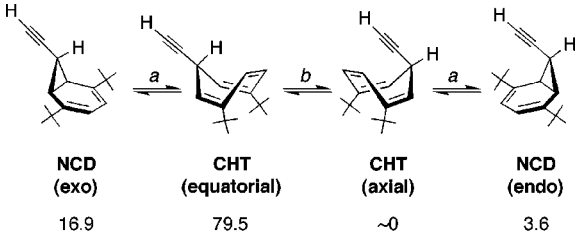
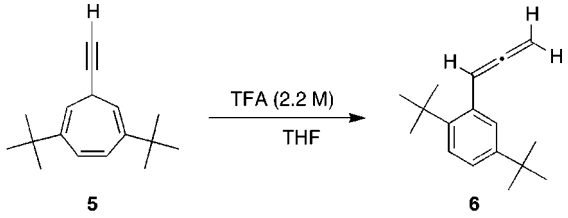


Figure 1. Equilibrium isomer populations (%) of 2,5-di-*tert*-butyl-7-ethynylcycloheptatriene **5** and its norcaradiene form (ref 7, at −120 °C in CS_2−CD_2Cl_2 3:1 v/v). a: valence tautomerism. b: ring inversion.

The CHT-NCD composition at equilibrium is a possible rate-controlling factor of the reaction shown in Scheme 2, and the increased population of the NCD form (20.5% at −120 °C, as determined by NMR[7]) for **5** should accelerate the acid-catalyzed rearrangement. Heating **5** in the presence of TFA (2.2 M) in THF at 60 °C resulted in quantitative isomerization to (2,5-di-*tert*-butylphenyl)allene **6** (Scheme 3), a product predicted by the mechanism shown in Scheme 2, in 4 h.

Scheme 3



For a kinetic study, the rearrangement of **1** and **5** was conducted in THF-d_8 in the presence of TFA (2.2 M) at 60 °C and monitored by ^{1}H NMR.[8] The reactions followed first-order kinetics, giving rate constants of 8.79×10^{-7} (**1**) and 3.22×10^{-4} (**5**) s^{-1}. Thus, an acceleration of the reaction by a factor of 370 was achieved.

With the expectation that the intermediate vinyl cation, **3** or its *tert*-butylated form, can be trapped by a nucleophile,[9] the products of the reaction of **1** and **5** in MeOH in the presence of HCl (0.1−0.5 M) at 60 °C were carefully analyzed. However, the reactions resulted in the complete conversion to phenylallenes **2** and **6**, with no methyl ether or chlorinated compounds being detected. The failure to trap cationic intermediates can be reasonably explained by the rapid conversion of the vinyl cation to the arenium ion due

(4) Compound **2** was identified by comparison of its ^{1}H and ^{13}C NMR spectra with those reported in the literature: Maercker, A.; Fischenich, J. *Tetrahedron* **1995**, *51*, 10209. Okuyama, T.; Izawa, K.; Fueno, T. *J. Am. Chem. Soc.* **1973**, *95*, 6749. Spectral data for compound **6**: colorless yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.50 (d, J = 2.3 Hz, 1H), 7.31 (d, J = 8.6 Hz, 1H), 7.17 (dd, J = 8.6, 2.3 Hz, 1H), 6.81 (t, J = 6.8 Hz, 1H), 5.09 (d, J = 6.8 Hz, 2H), 1.43 (s, 9H), 1.31 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 209.5 (C), 148.5 (C), 143.6 (C), 131.2 (C), 126.9 (CH), 125.8 (CH), 123.9 (CH), 94.4 (CH), 77.5 (CH_2), 35.0 (C), 34.2 (C), 31.4 (CH_3), 31.2 (CH_3). HRMS (FAB) calcd for $C_{17}H_{24}$: 228.1878; found: 228.1875.

(5) Cremer, D.; Dick, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 865.

(6) (a) Takeuchi, K.; Kitagawa, T.; Ueda, A.; Senzaki, Y.; Okamoto, K. *Tetrahedron* **1985**, *41*, 5455. (b) Takeuchi, K.; Fujimoto, H.; Kitagawa, T.; Fujii, H.; Okamoto, K. *J. Chem. Soc., Perkin Trans. 2* **1984**, 461. (c) Takeuchi, K.; Kitagawa, T.; Senzaki, Y.; Fujimoto, H.; Okamoto, K. *Chem. Lett.* **1983**, 69. (d) Takeuchi, K.; Kitagawa, T.; Toyama, T.; Okamoto, K. *J. Chem. Soc., Chem. Commun.* **1982**, 313. (e) Takeuchi, K.; Fujimoto, H.; Okamoto, K. *Tetrahedron Lett.* **1981**, *22*, 4981. (f) Takeuchi, K.; Arima, M.; Okamoto, K. *Tetrahedron Lett.* **1981**, *22*, 3081.

(7) Takeuchi, K.; Senzaki, Y.; Okamoto, K. *J. Chem. Soc., Chem. Commun.* **1984**, 111.

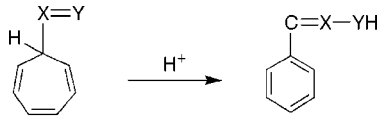
(8) The reaction solutions were prepared by dissolving **1** or **5** in a mixture of THF-d_8 and TFA (5:1 v/v). The solutions, containing 0.03−0.07 M of the substrate, were placed in a 5 mm o.d. NMR sample tube and were heated in a thermostated bath. At appropriate intervals the ^{1}H NMR spectra were recorded to determine the ratio of the starting compound and the product by peak integration.

(9) A review of the trapping of vinyl cation intermediates under solvolytic conditions: Kitamura, T.; Taniguchi, H.; Tsuno, Y. In *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; John Wiley & Sons: Chichester, 1997; chapter 7.

to resonance stabilization of the latter cation and the subsequent irreversible deprotonation to form an aromatic ring.[10,11]

The present result suggests the possible transformation of cycloheptatrienes bearing a directly attached multiple bond (X═Y) other than the ethynyl group into a benzene with a conjugated C═X−YH group under acidic conditions (Scheme 4). In search of the rearrangement of other 7-substituted

Scheme 4



cycloheptatrienes via a protonation−deprotonation mechanism, isomerization of vinyl and cyanocycloheptatrienes is now underway.

(10) DFT calculations (B3LYP/6-31G*) indicated that the rearrangement of **3** to **4** is exothermic by 2.3 kcal mol^{-1}.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (A) "Creation of Delocalized Electronic Systems" from the Ministry of Education, Science, Sports and Culture, Japan.

Supporting Information Available: Spectroscopic data for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) In connection with this finding, the ring opening of the norcaradienylmethyl cation has been proposed to explain the formation of styrene in the solvolysis of (2,4,6-cycloheptatrien-1-yl)methyl 3,5-dinitrobenzoate: Sargent, G. D.; Lowry, N.; Reich, S. D. *J. Am. Chem. Soc.* **1967**, *89*, 5985. See also Warner, P. M.; Lu, S.-L. *J. Am. Chem. Soc.* **1980**, *102*, 331. Thompson, G. L.; Heyd, W. E.; Paquette, L. A. *J. Am. Chem. Soc.* **1974**, *96*, 3177. It has been also reported that dialkoxy- and alkoxyamino-substituted norcaradienylmethyl cations rearrange to 1,1-disubstituted-2-phenylethyl cations under stable-ion conditions: Betz, W.; Daub, J.; Rapp, K. M. *Liebigs Ann. Chem.* **1974**, 2089.