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Thermal Migration of an Ethynyl Group From One Benzene Ring to Another by Reversible Vinylidene C-H Insertion[1]

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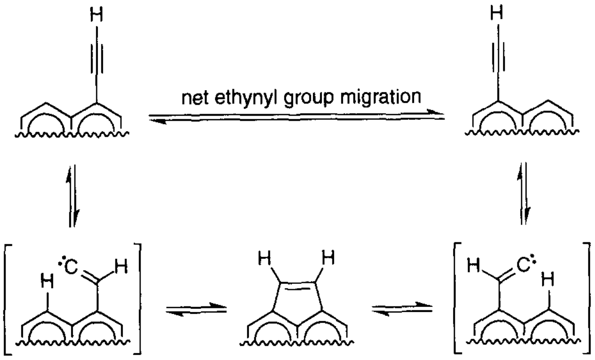
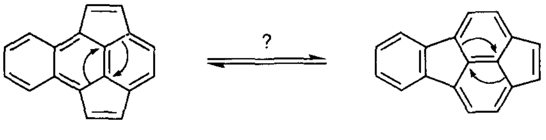
Abstract. Evidence is presented for the high temperature opening of a 5-membered ring by extrusion of a carbene (the reverse of a C-H bond insertion), which results in the net thermal migration of an ethynyl group from one benzene ring to another.

Thermal isomerization of a terminal alkyne to a vinylidene under flash vacuum pyrolysis (FVP) conditions and trapping of the transient carbene by intramolecular C-H insertion to form an etheno-bridged aromatic compound was first demonstrated by R. F. C. Brown *et al.* in the 1970s.[2] This high-temperature cyclization reaction is estimated to be exothermic by 15-20 kcal/mol overall,[3] and only the endothermic hydrogen shift has generally been regarded as reversible. We have now encountered a case, however, in which the vinylidene insertion step also appears to be reversible, and this reversibility leads to the net migration of an ethynyl group from one benzene ring to another along the edge of a polycyclic aromatic hydrocarbon ring system (eq 1).



(1)

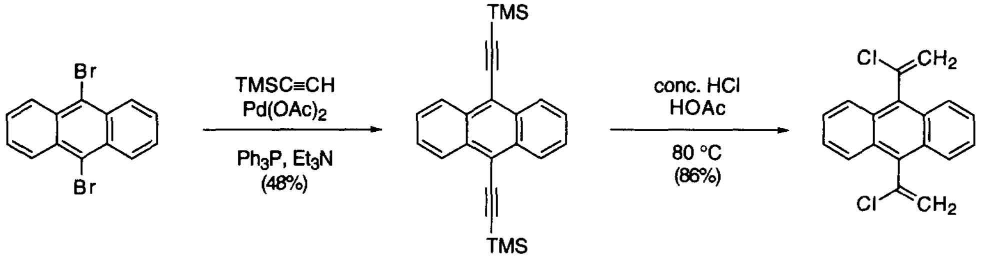
Extrusion of a carbene by de-insertion from a remote C-H bond is enormously endothermic,[3] of course, and reported examples are quite rare,[4] but every unimolecular reaction, in principle, must be reversible at sufficiently high temperatures. Accordingly, it seems reasonable that such ethynyl group migrations could play a significant role in the chemistry of hydrocarbons in flames, in the mechanism of carcinogen formation in smoke, and in the production of fullerenes and carbon nanotubes under high energy conditions *inter alia*. Our discovery of the title reaction occurred during the course of experiments designed to prepare the benzopyracylene **1**, a molecule we had hoped could be used to test the feasibility of the "Stone-Wales rearrangement[5]" (eq 2).



1 **2**

(2)

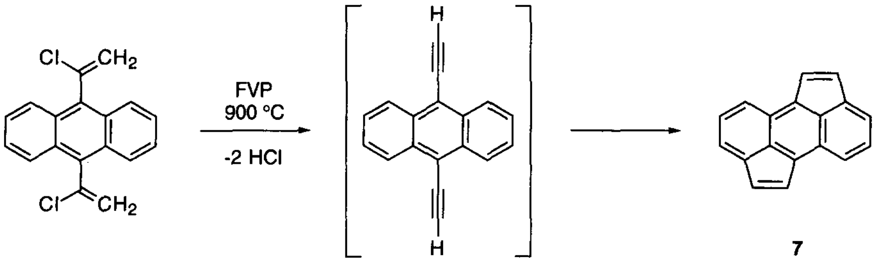
Palladium-mediated coupling of trimethylsilylacetylene with 9,10-dibromoanthracene (**3**) yielded the attractive synthetic precursor **4**.[6] Exposure of **4** to conc. HCl in glacial acetic acid (0.004:1, 80 °C, 3 h) then gave 9,10-*bis*(1-chlorovinyl)anthracene (**5**) (eq 3).[7]



3 **4** **5** (3)

We developed this latter synthetic transformation as an alternative to simple desilylation in order to avoid having to handle the unprotected 9,10-diethynylanthracene (**6**);[6] our previous experience with diethynyl-substituted aromatic hydrocarbons of this size had taught us that such compounds are ill-suited substrates for FVP because they polymerize too easily during sublimation.[8] Fortunately, we found that the 1-chlorovinyl group can be used as a "masked ethynyl group" in FVP,[9] since it loses HCl readily at high temperatures. The direct conversion of **4** to **5** represents a simple new method for preparing 1-chlorovinyl groups.

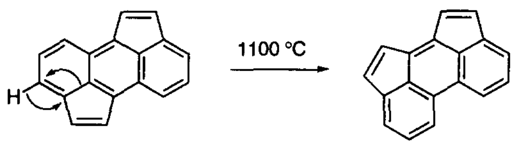
It was anticipated that thermal cyclization of **6**, generated *in situ* from **5**, would give the desired target compound (**1**) and/or the isomeric cyclopent[*hi*]aceanthrylene (**7**).[10] Unfortunately, when the FVP of **5** was conducted at 900 °C,[11] only the undesired isomer **7** was obtained (eq 4).



5 **6** **7** (4)

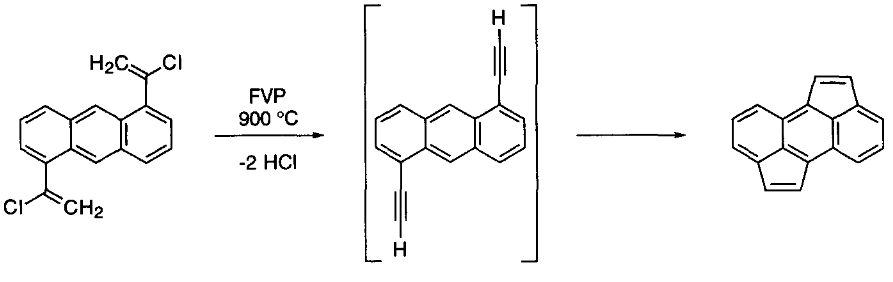
(**1** not obtained)

At higher temperatures, cyclopent[*hi*]acephenanthrylene (**8**) was also produced, at the expense of **7**.[10] We view the secondary formation of **8** as a straightforward example of the hydrogen-shift/benzene ring contraction rearrangement (eq 5), a well-precedented process discovered in our laboratory that is known to occur under FVP conditions at temperatures above 1000 °C.[12] Calculations[3] indicate that isomerization of the anthracene derivative **7** to the phenanthrene derivative **8** should be exothermic by approximately 8 kcal/mol.



7 **8** (5)

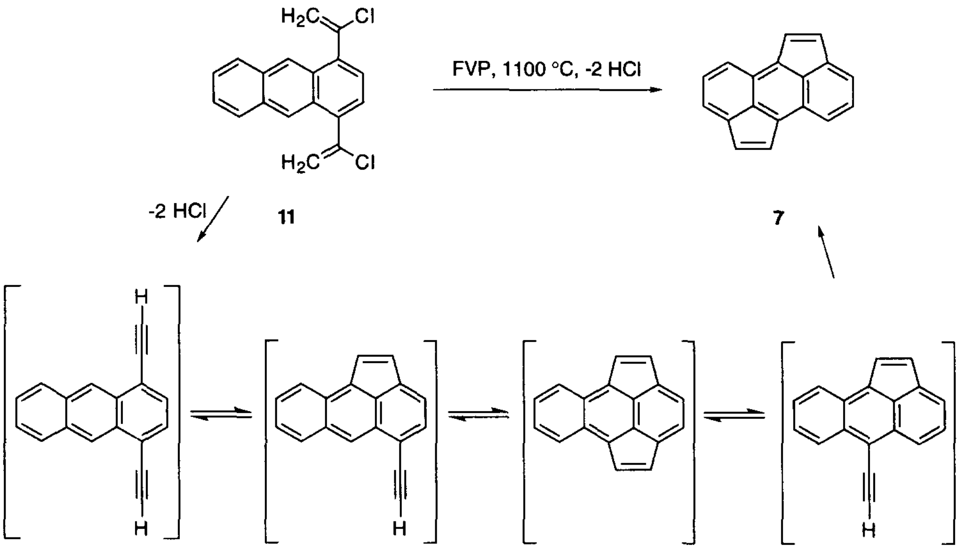
FVP of 1,5-*bis*(1-chlorovinyl)anthracene (**9**)[13] likewise gives **7** as the sole product at 900 °C, presumably via **10** (eq 6); a mixture of **7** and **8** was again obtained at 1100 °C.[10]



9 **10** **7**

(6)

Based on these rational results, we confidently assumed that FVP of 1,4-*bis*(1-chlorovinyl)anthracene (**11**)[13] would have no choice but to yield our desired target molecule, **1**, via **12**. With an oven temperature of 900 °C, both side chains did lose HCl; however, only one ethynyl group cyclized, and we isolated the ethynylaceanthrylene **13**.[14] At 1100 °C, no **13** survived, but instead of isolating the desired product, **1**, we were surprised to find the same mixture of **7** and **8** that had been formed from the isomeric precursors **5** and **9**! At no intermediate temperature were we ever able to detect even a trace of **1**. The most logical explanation for this unforeseen result is that **13** does actually cyclize to the expected product (**1**) but that the cyclized product is unstable under the reaction conditions, reopens the other way, and then proceeds on to **7** (eq 7). It is this isomerization of **13** to **14** via **1** that constitutes net migration of an ethynyl group from one benzene ring to the next (*cf.* eq 1).



11 **7**

12 **13** **1** **14**

(7)

The reason **1** suffers ring opening at these temperatures more easily than do most such compounds, we believe, stems from the strain energy of the pyracylene moiety. Ordinarily, cyclizations of aryl acetylenes to form etheno-bridged aromatic compounds are expected to be exothermic by 15-20 kcal/mol;[3] however, calculations place the heat of formation of **1** very close to that of the ring-open isomers **13** and **14**.[3] Thus, **1** can disappear almost as fast as it is formed, and the final cyclization of **14** to **7** (exothermic by 18-22 kcal/mol, according to theoretical calculations)[3] drains the equilibrium mixture into a deeper energy well.

In retrospect, the ability of an ethynyl group to migrate from one benzene ring to the next at high temperatures (eq 1) could have been predicted from energetic considerations and then demonstrated by rationally designed experiments. We make no claim for having predicted this process, but we have now begun to examine its scope by rationally designed experiments.

Acknowledgment. We thank the Department of Energy for financial support of this work.

References and Notes

(1) Presented at the Northeast Regional Meeting of the American Chemical Society, Burlington, VT, June, 1994 and at the Eighth International Symposium on Novel Aromatic Compounds, Braunschweig, Germany, August, 1995.

(2) Brown, R. F. C.; Eastwood, F. W.; Jackman, G. P. *Aust. J. Chem.* **1977**, *30*, 1757-67.

(3) Heats of formation (kcal/mol) have been calculated by semiempirical methods using Spartan software version 4.0 (Wavefunction, Inc., Irvine, CA 92715). For 1-ethynylnaphthalene —> acenaphthylene, ΔH_{calc} = -15.4 (AM1); -19.7 (PM3). For styrene —> benzene + vinylidene (*i.e.*, extrusion of vinylidene from a normal aromatic C-H bond) ΔH_{calc} = 96.2 kcal/mol (AM1); 92.7 (PM3). Additional $C_{18}H_{10}$ ΔH_f (AM1;PM3): **1** (158.0; 140.2), **7** (141.1; 124.2), **8** (133.0; 116.6), **13** (158.2; 145.4), and **14** (159.1; 146.3).

(4) The only prior example of a carbene extrusion from a remote (non-adjacent) C-H bond that we know of is the one reported by Adeney, M.; Brown, R. F. C.; Coulston, K. J.; Eastwood, F. W.; James, I. W. *Aust. J. Chem.* **1991**, *44*, 967-80; Brown, R. F. C.; Eastwood, F. W.; Wong, N. R. *Tetrahedron Lett.* **1993**, *34*, 1223-6.

(5) Stone, A. J.; Wales, D. J. *Chem. Phys. Lett.* **1986**, *128*, 501-3; Murry, R. L.; Strout, D. L.; Odom, G. K.; Scuseria, G. E. *Nature* **1993**, *366*, 665-7; Hawkins, J. M.; Nambu, M.; Meyer, A. *J. Am. Chem. Soc.* **1994**, *116*, 7642-5 and references cited therein.

(6) Compounds **4** and **6** were first reported by Kobayashi, E.; Jiang, J.; Furukawa, J. *Polym. J.* **1990**, *22*, 266-73; Kobayashi, E.; Jiang, J.; Ohta, H.; Furukawa, J. *J. Polym. Sci., A: Polym. Chem.* **1990**, *28*, 2641-50.

(7) The three isomeric *bis*(1-chlorovinyl)anthracenes **5** (mp 225-6 °C), **9** (mp 126-7 °C), and **11** (mp 100-1 °C) were characterized by ^1H NMR, ^{13}C NMR, and high resolution mass spectroscopy.

(8) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082-4.

(9) Scott, L. T.; Cheng, P.-C.; Bratcher, M. S. *Seventh International Symposium on Novel Aromatic Compounds*, abstr. no. 64, Victoria, British Columbia, Canada, July 19-24, 1992; Cheng, P.-C., M.S. thesis, University of Nevada, Reno, 1992; Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291-300 and references cited therein. See also Jenneskens, L. W.; Sarobe, M.; Zwikker, J. W. *Pure Appl. Chem.* **1996**, *68*, 219-24.

(10) Formation of **7** by FVP of **9** and isomerization of **7** to **8** were discovered independently by Sarobe, M.; Snoeijer, J. D.; Jenneskens, L. W.; Zwikker, J. W.; Wesseling, J. *Tetrahedron Lett.* **1995**, *36*, 9565-6.

(11) Pyrolyses: 50 mg samples, unpacked tube, pump with N_2 carrier gas leak, net pressure 1 torr.

(12) Scott, L. T.; Roelofs, N. H. *J. Am. Chem. Soc.* **1987**, *109*, 5461-5; Scott, L. T.; Roelofs, N. H. *Tetrahedron Lett.* **1988**, *29*, 6857-60; Scott, L. T.; Hashemi, M. M.; Schultz, T. H.; Wallace, M. B. *J. Am. Chem. Soc.* **1991**, *113*, 9692-3.

(13) (a) For the syntheses of 1,5- and 1,4-*bis*(1-chlorovinyl)anthracene (**9** and **11**), trimethylsilylacetylene was deprotonated with ethylmagnesium bromide in THF and coupled with 1,5-dichloroanthracene[13b] or 1,4-dichloroanthracene[13c] under the catalytic influence of $Ni(acac)_2$[13d] (65 °C, 24 h, 87% and 90% yield, resp.). The resulting *bis*(trimethylsilylethynyl)anthracenes were then converted directly to the *bis*(1-chlorovinyl) derivatives with conc. HCl in acetic acid (0.004:1, 80 °C, 3 h, 81% and 90% yield, resp.).[7] (b) House, H. O.; Ghali, N. I.; Haack, J. L.; VanDerveer, D. *J. Org. Chem.* **1980**, *45*, 1807-17. (c) Krapcho, A. P.; Getahun, Z. *Synth. Commun.* **1985**, *15*, 907-10. (d) Katz, H. E. *J. Org. Chem.* **1989**, *54*, 2179-83.

(14) Hydrocarbon **13** was identified only by ^1H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.22 (d, 1H, J = 8.6 Hz), 8.12 (d, 1H, J = 8.8 Hz), 7.79 (d, 1H, J = 6.7 Hz), 7.72 (d, 1H, J = 6.8 Hz), 7.60 (d, 1H, J = 5.1 Hz), 7.59 (t, 1H, J = 7.3 Hz), 7.47 (t, 1H, J = 7.2 Hz), 7.06 (d, 1H, J = 5.4 Hz), 3.61 (s, 1H).

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