Pergamon

Tetrahedron Letters 43 (2002) 5269–5272

TETRAHEDRON
LETTERS

Flash vacuum pyrolysis of 1,6-diphenyl-1,5-hexadien-3-ynes: tandem diaryldienyne cyclizations to form chrysene

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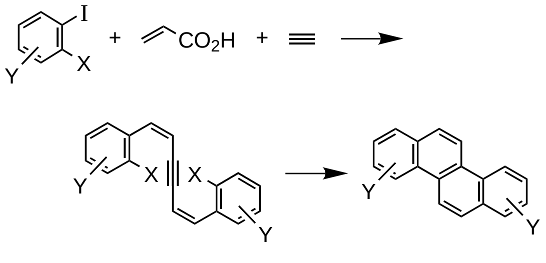
Received 17 April 2002; revised 30 May 2002; accepted 31 May 2002

Abstract—Flash vacuum pyrolysis of 1,6-diphenyl-1,5-hexadien-3-yne at 1000°C and its bromo derivative at 800°C yielded chrysene as the major product through tandem diaryldienyne cyclizations. © 2002 Elsevier Science Ltd. All rights reserved.

Cycloaromatization of 6π electron systems containing one or two triple bond(s) such as diethynylarenes (i.e. Bergman cyclization)[1] and aryl enynes[2,3] has been attracting a great deal of interest from mechanistic, synthetic, and biological points of view. Recently, ingenious utilization of these and related reactions has been developed to construct highly conjugated polymers and polycyclic aromatic hydrocarbons (PAHs) which have potential applications in electronic and photonic materials. These include enediyne cyclization to form polyphenylenes[4] and linear acenes,[5] double enediyne cyclization to form perylene,[6] oxidative cyclization of bis(biaryl)acetylenes to form dibenzo[*g*,*p*]chrysenes,[7] and electrophilic cyclization of ethynyl biphenyls to furnish dibenzoanthracene derivatives.[8] As a novel variant of such methods we planned to develop the cycloaromatization reaction of diaryldienynes to form chrysene derivatives by tandem cyclizations, as shown in Scheme 1. In view of the convenient assembly of the aryldienyne units from aryl, vinyl and alkyne fragments based on the Heck and Sonogashira type coupling reactions, the overall transformation would provide a versatile entry into chrysene derivatives. As a prototype of the reaction in Scheme 1, we investigated the cyclization of 1,6-diphenyl-1,5-hexadien-3-yne (**1a**) and 1-(2-bromophenyl)-6-phenyl-1,5-hexadien-3-yne (**1b**) to chrysene (**2**) under thermal conditions. Thermal[2] and photochemical[3] cycloaromatizations of aryl enynes as well as photochemical cyclization of diarylethenes (i.e. stilbene cyclization)[9] have been well documented.[10] Photochemical cyclization of 1,6-diphenyl-1,3,5-hexatriene to **2**, which includes tandem stilbene cyclizations, was also reported to occur, albeit with low efficiency.[11] However, to our knowledge, tandem diaryldienyne cyclization has not been known in spite of its versatility and mechanistic interest. In addition, thermal reactions of highly unsaturated molecules to form PAHs are important in connection with not only our own research on the polyyne cyclization to form carbon cages[12] but also the occurrence of PAHs in circumstellar envelopes.[13]



Scheme 1.

Diaryldienynes **1a** and **1b** were prepared from the corresponding (*Z*)-bromostylenes **3a**[14] and **3b**[15] by (i) the first Sonogashira coupling reaction with (trimethylsilyl)acetylene followed by deprotection to give enynes **4a** and **4b**, respectively, and (ii) the second Sonogashira coupling reaction of **4a** and **4b** with **3a**, as shown in Scheme 2. The products **1a** and **1b**[16] contained small amounts of (*E*,*E*)-[17] and (*E*,*Z*)-isomers. Although pure (*Z*,*Z*)-isomers **1a** and **1b** were obtained by preparative HPLC, the mixtures containing small amounts of the isomers may be used in their photolysis and pyrolysis since under both reaction conditions *cis*–*trans* isomer-

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Keywords: flash vacuum pyrolysis; aryl enynes; cyclizations; chrysene.

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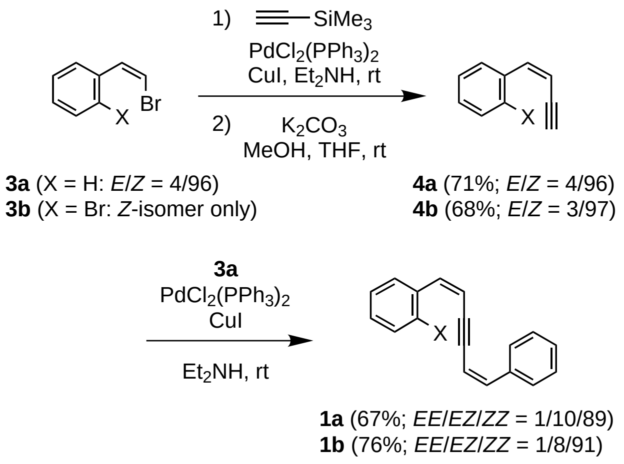
PII: S0040-4039(02)01062-6



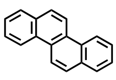
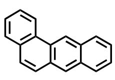
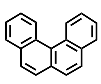
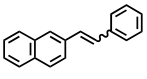
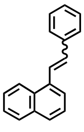
Scheme 2.

ization takes place. *o*-Bromo-2-bromostylene (**3b**) was prepared stereoselectively ($E/Z = 3/97$) from *o*-bromoiodobenzene by (i) the Heck reaction with acrylic acid, (ii) bromination, and (iii) decarboxybromination according to the same procedures for the preparation of **3a** with slight modification.[14,15]

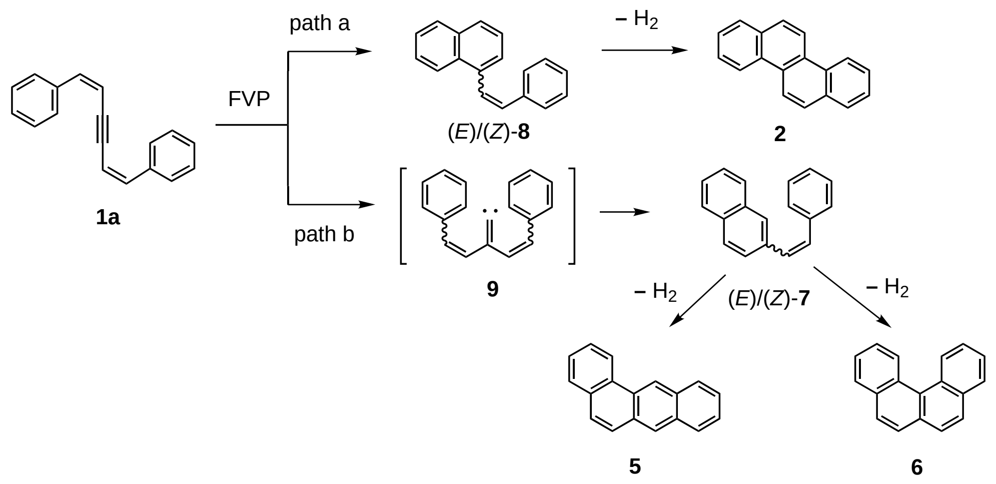
In contrast to the aromatic enynes which underwent facile cycloaromatization photochemically,[3] attempts to effect photochemical cyclization of **1a** and **1b** by irradiation of their cyclohexane solutions with a high-pressure mercury lamp resulted in only E/Z isomerization of the double bond, yielding a mixture of **1a** or **1b** and its (*E*,*Z*)- and (*E*,*E*)-isomers.[17,18] At the photostationary state,[19] the yields of the isomers were determined as follows by GC using appropriate internal standards: (*E*,*E*)-isomer:(*E*,*Z*)-isomer:**1a** = 43:43:14; (*E*,*E*)-isomer: two (*E*,*Z*)-isomers:**1b** = 39:24:21:16. However, in both cases, (*Z*,*Z*)- and (*E*,*Z*)-isomers were converted to the respective (*E*,*E*)-isomer by allowing them to stand for a few weeks without shielding from ordinary room light.

Then flash vacuum pyrolysis (FVP) of **1a** was carried out at 800 and 1000°C under a slow stream of nitrogen. The product distribution is listed in Table 1. The products, chrysene (**2**), benz[*a*]anthracene (**5**), benzo[*c*]-phenanthrene (**6**), 2-styrylnaphthalenes (*E*)-**7** and (*Z*)-**7**, and 1-styrylnaphthalenes (*E*)-**8** and (*Z*)-**8**, were identified by comparison of their GC, GC/MS, and ^{1}H NMR spectra with those of authentic samples or with the reported data.[20,21] At 800°C, 2-styrylnaphthalene (*E*)-**7** was obtained as the major product together with small amounts of PAHs **2**, **5** and **6**. By contrast, pyrolysis at 1000°C gave chrysene (**2**) as the major product with moderate increase of **5** and **6** and apparent decrease of (*E*)-**7**. The formation of **2** can be explained in terms of cycloaromatization of the phenyl enyne moiety to form 1-styrylnaphthalene **8**, either by concerted 6π electrocyclization followed by hydrogen shift, or radical species-catalyzed cyclization mechanism,[2] and subsequent stilbene cyclization (Scheme 3, path a). The formation of (*E*)-**7** is ascribed to acetylene-to-vinylidene rearrangement followed by C–H insertion.[2] Subsequent stilbene cyclization of (*Z*)-**7** would give PAHs **5** and **6** (path b; Scheme 3). A separate experiment on pyrolysis of PAH **5** at 1000°C (1 mmHg) resulted in the recovery of the starting material without formation of chrysene (**2**).[22] On the other hand, PAH **6**

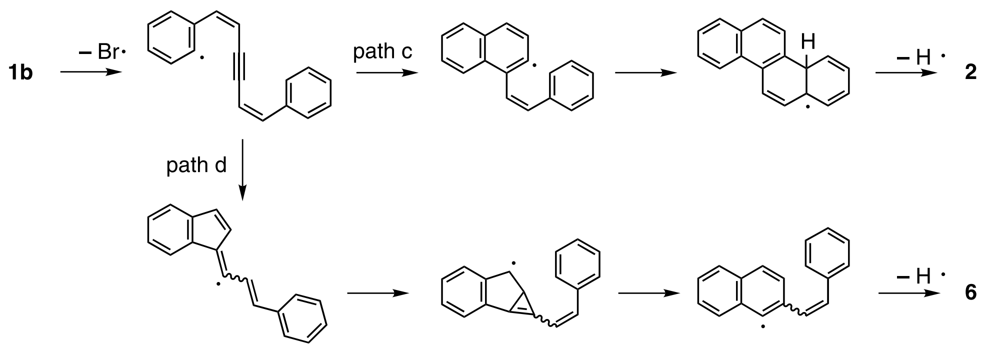
Table 1. Flash vacuum pyrolysis of **1a** and **1b**

			Product distribution (%)[c]						
Substrate	Temp[a] (°C)	Balance[b] (%)	 **2**	 **5**	 **6**	 (*E*) / (*Z*)-**7**	 (*E*) / (*Z*)-**8**	**1a** or **1b**/ (*E*, *E*)-isomer/ (*E*, *Z*)-isomer(s)[d]	Unidentified Products
1a	800	51	9	2	3	29 / 5	13 / 3	3 / 7 / trace	26
	1000	33	27	15	12	3 / 1	1 / –	–	41
1b	650	58	61	2	10	–	–	2 / 4 / 6	15
	800	58	73	6	21	–	–	–	–

[a] The reactions were carried out at about 1 mmHg under a slow stream of nitrogen which was introduced through a capillary into the pyrolysis tube. [b] Percent ratio of the weight of products relative to the starting material which passed through the heated zone of the pyrolysis tube. Since the loss of HBr from **1b** would result in a 26% reduction of the weight, the mole-based material balance in the reaction of **1b** should be regarded at least more than 50%. [c] Based on GC peak areas. [d] Two (*E*, *Z*)-isomers of **1b** were detected by GC analysis.



Scheme 3.



Scheme 4.

was reported to behave differently depending on the temperature and pressure. Thus, **6** is inert at 950°C (0.01 mmHg) while it isomerized to benzo[*ghi*]-fluoranthene and cyclopenta[*cd*]pyrene at 1050°C (0.1 mmHg),[23,24] ruling out the possible equilibration between the PAHs **2** and **5** as well as **6**. In other words, **2** is a kinetically favored product of pyrolysis at 1000°C. It is therefore deduced that, at low temperature, the carbene route (path b) predominates in analogy with the simple systems.[2] At higher temperature, contribution of path a may be increased, most probably because of the increase of the amount of radical species which catalytically induces the cyclization through path a.

FVP of the bromo derivative **1b**, on the other hand, gave chrysene (**2**) as the major product both at 650 and 800°C. Evidently, initial C–Br bond cleavage and subsequent radical cyclization (Scheme 4, path c) facilitated the formation of **2** in comparison with the enyne cyclization pathway (cf. Scheme 3, path a),[10,23] even though the competitive carbene route (path b) to form **5** and **6** was not completely suppressed. Also, **6** might be formed by an alternative radical cyclization process[2] (Scheme 4, path d) because the ratio of **6** relative to **5** was large compared to the result in the pyrolysis of **1a**.

In conclusion, high temperature FVP of dienynes **1a** and **1b** gave chrysene (**2**) as the major product presumably through tandem aryl enyne–stilbene cyclization and radical cyclization, respectively. Further work to effect cyclization under mild conditions from appropriately functionalized starting materials is in progress in our laboratories.

Acknowledgements

This work was partially supported by Grants-in-Aid from the Ministry of Education, Science, Sports and Culture of Japan. The authors are grateful to Professor M. Yasuda (Miyazaki University) for providing copies of ^{1}H NMR spectra of 1- and 2-styrylnaphthalenes and a sample of the latter and to Professor Y. Aso (Hiroshima University) for his advice regarding FVP. Y.T. thanks Shin-Etsu Chemicals Co. for a generous gift of organosilicon reagents.

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16. Selected data for **1a** ((*Z*,*Z*)-isomer): mp 58–60°C; ^{1}H NMR (300 MHz, $CDCl_3$, 30°C) (the non-first-order coupling constants were elucidated by simulation) δ 7.88–7.85 (m, 4H), 7.35–7.27 (m, 6H), 6.69–6.64 (m, $J=11.6$, 1.6, −0.7 Hz, 2H), 5.96–5.91 (m, $J=11.6$, 1.6, −0.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 30°C) δ 138.6 (s), 136.4 (d), 128.6 (d), 128.5 (d), 128.4 (d), 107.5 (d), 94.6 (s); IR (KBr) 3059, 3025, 1595, 1491, 1449, 1417, 919, 789, 690 cm^{-1}; UV $\lambda_{\max}$ (log ε) 360 (sh, 3.80), 337 (4.47), 262 (4.41) nm; MS (EI) *m*/*z* 230 (M^+). Anal. calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.50; H, 6.05%. For **1b** ((*Z*,*Z*)-isomer): ^{1}H NMR (300 MHz, $CDCl_3$, 30°C) δ 8.29 (dd, $J=6.0$, 1.5 Hz, 1H), 7.81–7.77 (m, 2H), 7.59 (dd, $J=6.0$, 1.2 Hz, 1H), 7.29–7.19 (m, 4H), 7.13 (ddd, $J=7.8$, 7.5, 1.5 Hz, 1H), 6.99 (d, $J=12.0$ Hz, 1H), 6.65 (d, $J=12.0$ Hz, 1H), 6.05 (dd, $J=12.0$, 3.0 Hz, 1H), 5.86 (dd, $J=12.0$, 3.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 30°C) δ 139.0 (d), 137.3 (d), 136.3 (s), 135.9 (s), 132.8 (d), 129.7 (d), 129.6 (d), 128.6 (d), 128.5 (d), 128.3 (d), 127.2 (d), 124.1 (s), 109.9 (d), 107.2 (d), 94.5 (s), 93.3 (s); IR (neat) 3061, 3023, 2162, 1587, 1492, 1466, 1447, 1434, 1416, 1023, 771, 741, 690 cm^{-1}; UV $\lambda_{\max}$ (log ε) 333 (4.30), 263 (4.28), 254 (sh, 4.26) nm; MS (EI) *m*/*z* 310, 308 (M^+), 229 (M^+−Br), 228 (M^+−HBr). HRMS (EI) calcd for $C_{18}H_{13}Br$: 310.0182, 308.0201. Found: 310.0221, 308.0145.
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