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Communications

An Interesting Benzyne-Mediated Annulation Leading to Benzo[*a*]pyrene

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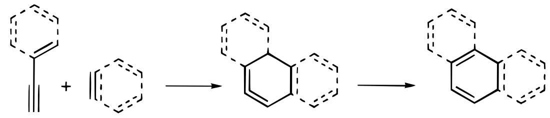
The Diels−Alder reaction—one of the most useful synthetic transformations in organic synthesis—has been the subject of a huge amount of theoretical and experimental work in the last 10 years. In spite of this, the closely related cycloaddition reaction between a conjugated enyne and a dienophile, known as the dehydro Diels−Alder reaction (DDAR), remains relatively unknown.[1] Scheme 1 shows a general representation of this reaction (solid lines), assuming a concerted mechanism through an allene intermediate (an acid-catalyzed stepwise mechanism has been proposed for some of these reactions).

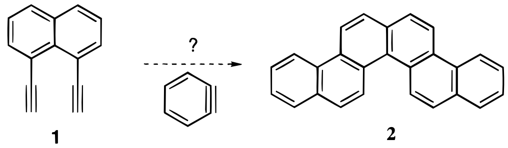
After more than 10 years of working on the synthesis of natural products by means of Diels−Alder reactions between styrene derivatives and arynes,[2] we focused our attention on the corresponding DDAR between arylalkynes and arynes (Scheme 1).[3] In view of the recent advances made in the synthesis of arylacetylenes, and the new procedures available for the generation of benzyne, we envisaged that the DDAR might be useful for the synthesis of policyclic aromatic hydrocarbons. To test this hypothesis, we examined the reaction between the readily available arylalkyne, 1,8-diethynylnaphthalene (**1**), and benzyne, which we expected would afford naphtho[1,2-*c*]chrysene (**2**) via a double DDAR (Scheme 2). We also considered the possibility that a formal [2 + 2 + 2] cycloaddition between the alkyne units and benzyne might occur since intramolecular interactions between the triple bonds of compound **1** have been reported.[4]

Diyne **1** was made from 1,8-naphthalene diiodide (**3**) as shown in Scheme 3. Transformation of **3** into **5** was accomplished either in two steps through iodoalkyne **4** or in a one-pot reaction, in both cases using Pd(PPh$_3$)$_2$Cl$_2$ in the presence of Et$_2$NH and Cu to catalyze the coupling reaction between the iodides and (trimethylsilyl)acetylene. Finally, **5** was desilylated by treatment with *n*-Bu$_4$NF/THF to yield **1** in 95% yield.[5]

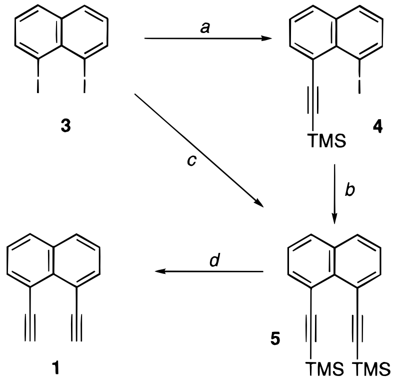
Scheme 1



Scheme 2



Scheme 3[a]



[a] Key: (a) (PH$_3$P)$_2$PdCl$_2$, CuI, 1.1 equiv of HCCTMS, Et$_2$NH, 58%; (b) (Ph$_3$P)$_2$PdCl$_2$, CuI, 2.0 equiv of HCC−TMS, Et$_2$NH, 42%; (c) (Ph$_3$P)$_2$PdCl$_2$, CuI, 2.8 equiv of HCC−TMS, Et$_2$NH, 30%; (d) *n*-Bu$_4$N$^+$F$^-$, THF, 95%.

For the DDAR of **1** with benzyne, the latter was generated by two alternative procedures: firstly (method A), by the thermal decomposition of benzenediazonium 2-carboxylate in a refluxing 1,2-dichloroethane solution of diyne **1**;[6] later (method B), by room-temperature treatment of 2-(trimethylsilyl)phenyl triflate with fluoride ion[7] in a THF solution of **1**. In both cases, benzopyrene (**6**) was obtained as the only isolable product, in 23% yield by method A and in 30% yield by method B.

Scheme 4 shows a possible mechanism for this unexpected transformation. The first step is a DDAR affording strained cyclic allene **7**.[8,9] Strained 1,2-cyclohexadienes have previously been proposed as intermediates

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[1] (a) Kloetgel, M. C.; Holmes, H. L. *Org. React.* **1948**, *4*, 60. (b) Onischenko, A. S. *Diene Synthesis*; Daniel Dave & Co.: New York, 1964. (c) Butz, L. W.; Gaddis, A. M.; Butz, E. J. W.; Davis, R. E. *J. Org. Chem.* **1969**, *34*, 1857. (d) Whitlock, H. W., Jr.; Wu, E. M.; Withlock, B. J. *J. Org. Chem.* **1969**, *34*, 1857. (e) Miller, B.; Ionescu, D. *Tetrahedron Lett.* **1994**, *35*, 6615. (f) Danheiser, R. L.; Gould, A. E.; Fernández de la Pradilla, R.; Helgason, A. L. *J. Org. Chem.* **1994**, *59*, 5514. (g) Burrell, R. C. Daoust, K. J.; Bradley, A. Z.; DiRico, K. J.; Johnson, R.P. *J. Am. Chem. Soc.* **1996**, *118*, 4218.

[2] See, for example: Atanes, N.; Castedo, L.; Guitián, E.; Saá, C.; Saá, J. M.; Suau, R. *J. Org. Chem.* **1991**, *56*, 2984.

[3] For previous examples of this reaction see: (a) Dyke, S. F.; Marshall, A. R.; Watson, J. P. *Tetrahedron* **1966**, *22*, 2515. (b) Stiles, M.; Burckhardt, U.; Haag, A. *J. Org. Chem.* **1962**, *27*, 4715.

[4] Staab, H. A.; Nissen, A; Ipaktschi, J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 226.

[5] For the preparation of **1** by Pd-catalyzed reactions of 1,8-diiodonaphthalene and acetylene, see: Badrieh, Y.; Blum, J.; Schumann, H. *J. Mol. Catal.* **1994**, *90*, 231. Compound **1** has also been prepared by dehydrohalogenation of 1,8-bis(1′,2′-dibromoethyl)naphthalene; see: Mitchell, R. H.; Sondheimer, F. *Tetrahedron* **1968**, *24*, 1397.

[6] A description of the experimental procedure can be found in ref 2.

[7] Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, 1211.

[8] For a comprehensive review of strained cyclic cumulenes see: Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111.

[9] The actual structure of compounds formulated as strained allene intermediates is not obvious. The spatial structure and electronic distribution of these strained intermediates has been studied. See: (a) Angus, R. O., Jr.; Schmidt, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 532. (b) Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 476.

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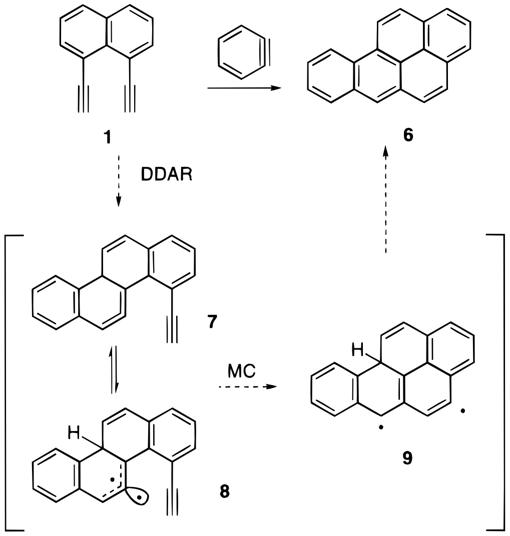
Scheme 4



either in DDAR,[1] in base-promoted elimination of HBr or HCl from 1-cyclohexenylhalides,[10] in the reaction of 1,6-dibromocyclohexene with magnesium,[11] in the pyrolysis of 6-(chlorocarbonyl)bicyclo[3.1.0]hexane[12] or 6-bromo-6-(trimethyltin)bicycl[3.1.0]hexane,[13] in the fluoride ion-promoted elimination of TMS and Br from 1-bromo-6-(trimethylsilyl)cyclohexene,[14] and in the reaction of 6,6-dibromobicyclo[3.1.0]hexane with MeLi.[15] Although the formation of such strained allenes appears intuitively to be a thermodynamically unfavorable process, enthalpy calculations show that this is not always the case.[16] Subsequently, instead of formation of the expected naphtho[1,2-*c*]chrysene (**2**) by a second DDAR between allenyne **7** and benzyne, either **7** or the biradical **8** (a similar equilibrium between a cyclic allene intermediate and a biradical has been postulated for a related DDAR)[1f] cyclizes to a σ, π-biradical **9**, which undergoes hydrogen migration to afford **6**. The cyclization step can be considered as a Myers' cyclization (MC),[17] but with some particular features: the starting material is a strained cyclic allene intermediate rather than a stable, isolable compound,[18] and, whereas in a typical Myers' cyclization the σ, π-biradical intermediate abstracts a hydrogen from a donor molecule such as a solvent or 1,4-cyclohexadiene, in this case the σ, π-biradical rearranges to the final product in a process involving either an intermolecular hydrogen abstraction or, quite possibly, an intramolecular hydrogen migration step.

To the best of our knowledge, this is the first example of a sequential DDAR−Myers cyclization. Further work to investigate the scope of this transformation is in progress.

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Supporting Information Available: Experimental procedures and spectral data for all new compounds (3 pages).

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(11) Boyden, F. M. Ph.D. Dissertation, University of the Pacific, Stockton, California, 1969.

(12) Wentrup, C.; Gross, G.; Maquestiau, A.; Flammang, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 542.

(13) Runge, A; Sander, W. *Tetrahedron Lett.* **1986**, *48*, 5835.

(14) Shakespeare, W. C.; Johnson, R. P. *J. Am Chem. Soc.* **1990**, *112*, 8578.

(15) (a) Moore, W. R.; Moser, W. R. *J. Am. Chem. Soc.* **1970**, *92*, 5469. (b) Christl, M.; Braun, M.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 473.

(16) Reference 1f reports an estimated $\Delta H_f = -29.7$ kcal/mol for an allene intermediate in a related DDAR. A $\Delta H_f = -25.4$ kcal/mol was obtained from *ab initio* calculations for a similar reaction described in ref 1g.

(17) (a) Myers, A. G.; Kuo, E. Y.; Finney, S. N. *J. Am. Chem. Soc.* **1989**, *111*, 8057. (b) Myers, A. G.; Dragovich, P. S.; Kuo, E. Y. *J. Am. Chem. Soc.* **1992**, *114*, 9369.

(18) For an example of Myers' cyclization of allenes generated *in situ*, see: (a) Ohe, K.; Kojima, M.; Yonehara, K.; Uemura, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1823. (b) Grissom, J. W.; Klingberg, D.; Huang, D.; Slattery, B. J. *J. Org. Chem.* **1997**, *62*, 603.