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A new rearrangement of cyclic allenes via 1,2-dehydro[10]annulenes: formation of benzo[*c*]fluorenones

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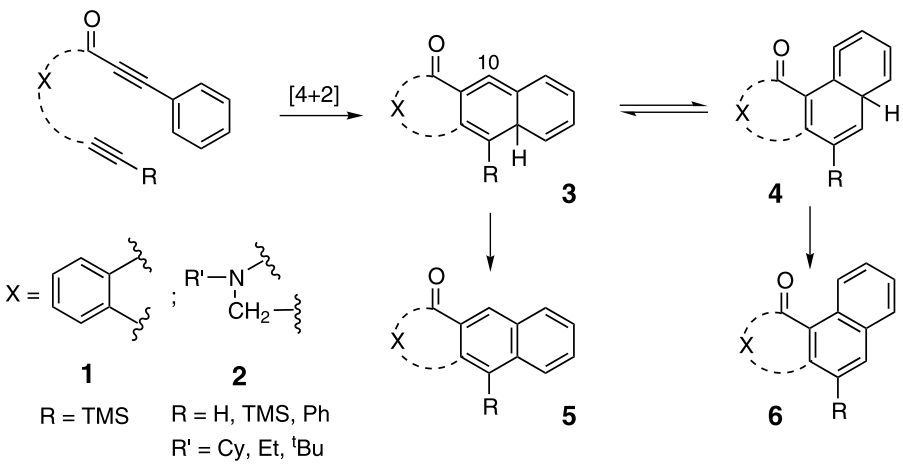
Abstract—A new rearrangement of cyclic allenes giving benzo[*c*]fluorenones was observed when studying intramolecular dehydro Diels–Alder reactions of silyl-substituted alkynes with arenynes (aryldiacetylenes). © 2002 Elsevier Science Ltd. All rights reserved.

We[1,2] have previously shown that the intramolecular dehydro Diels–Alder reaction[3] of alkynes with arenynes (aryldiacetylenes) provides an interesting new route to the tetracyclic nucleus of the benzo[*b*]fluorene antibiotics.[4] Its key step is the [4+2] cycloaddition of an alkyne unit linked to an arylacetylene, which involves the formation of a strained cyclic allene intermediate.[2]

Since then it has been found in work using starting aryldiacetylenes **1**[5] and **2**[6] that the expected aromatic product **5** may be accompanied by variable amounts of its isomer **6** (Scheme 1), possibly because the initial strained cyclic allene intermediate **3** isomerizes via 1,2-dehydro[10]annulene to cyclic allene **4**, which finally rearranges to **6**.[6] Here we report the results of an investigation of whether the intramolecular dehydro Diels–Alder reactions of the closely related aryldiacetylenes **8**,[7] which in our earlier work[2] had given benzo[*b*]fluorenones **9** almost exclusively, would also give isomers **10** if reacted under appropriate conditions.

In our previous work,[2] thermolysis of **8a** in commercial grade toluene gave benzo[*b*]fluorenone **9a** in 85% yield together with tiny amounts of an unidentified product. When we heated a solution of **8a** in dry, freshly distilled benzene at 150°C for 12 h, an inseparable mixture of



Scheme 1.

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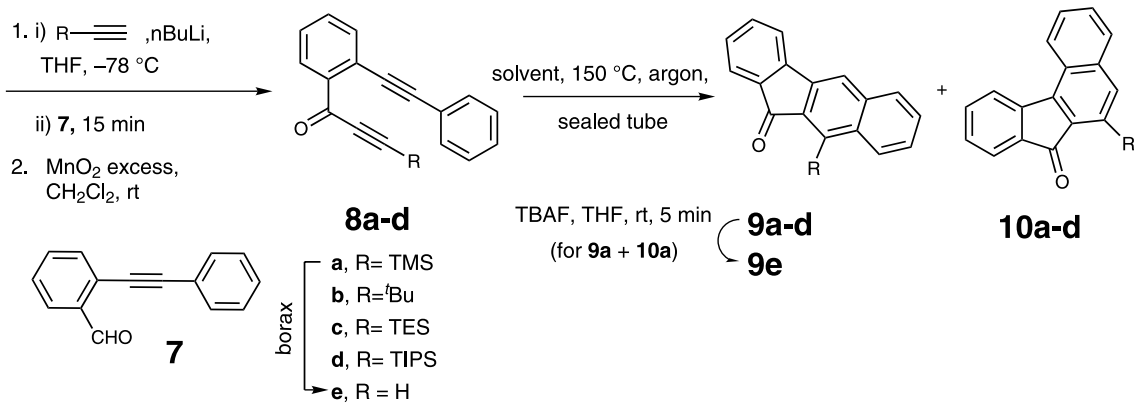
two silylated compounds in 2.2:1 ratio was obtained. Upon removal of the TMS group by reaction with tetrabutylammonium fluoride solution in THF at room temperature for a short time,[10] only one of the isomers reacted, allowing isolation of the desilylated benzo[*b*]fluorenone **9e**[2] and the benzo[*c*]fluorenone **10a**[11,12] in 61% and 28% yields, respectively (Scheme 2). The structure of **10a** was unambiguously established by an X-ray analysis.[13]

When the rather unstable aryldiacetylene **8e** (R = H), obtained by desilylation of **8a** (aqueous borax, MeOH, rt),[2] was heated under the same conditions as **8a** (benzene, 150°C, 12 h), it gave only the expected benzo[*b*]fluorenone **9e** in 70% yield (Table 1, entry 10), suggesting that the presence of a bulky terminal substituent on the alkyne was necessary for rearrangement of the cyclic allene intermediate **11** to the "angular" cyclic allene **14** via 1,2-dehydro[10]annulenes **12** and **13** (Scheme 3);[14] the dependence of this process on the R-group of **8** would be in keeping with our previous results with silyl-substituted phenylpropiolamides **2**.[6] In an attempt to increase the yield of **10**, we therefore carried out experiments with **8b–d**,[7] which have different bulky groups on the alkyne terminus (Table 1). However, the *t*-butyl derivative **8b** not only gave very little **10b** but also cyclized very slowly (suggesting that R had to be a silyl group); the TES derivative **8c** gave more or less the same 2:1 ratio of **9** to **10** as **8a**; and the sterically more compromised TIPS derivative **8d** failed to cyclize.[15]

Next we investigated the role of the solvent in this type of reaction, an aspect to which little attention had hitherto been paid. First we found that the use of toluene instead of benzene caused little difference in the results (Table 1, entries 1 and 2), showing that the presence of possible radical hydrogen donors plays at most a minor role in the final aromatization step. Then we used a variety of solvents capable of interfering with the allene intermediates. With triethylamine, the benzo[*b*]fluorenone was isolated as the only product in quantitative yield and extremely high purity (entry 3); this is attributed to its acting as a catalytic base for the aromatization step **11**→**9**, thus precluding both the opening of **11** to the annulene **12** and any side reactions of the allene.

With the protic solvent *i*PrOH there was again a good yield of **9** but no **10** (entry 4); probably because it allows aromatization to **9** by proton transfer.[2] When

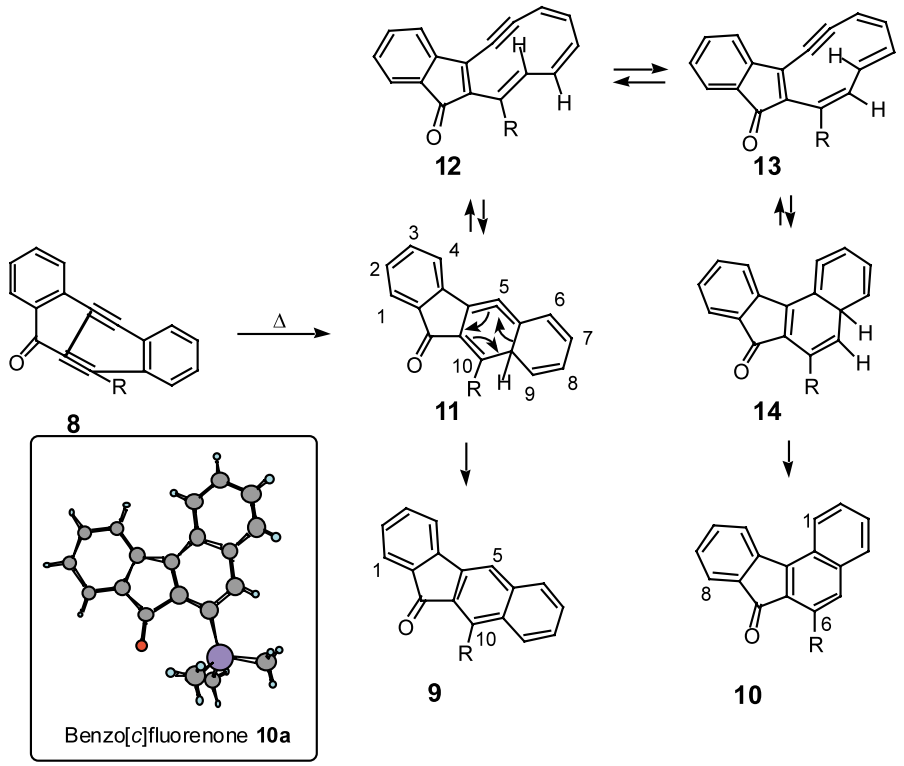


Scheme 2.

Table 1. Thermolysis of aryldiacetylenes **8**[a]

Entry	Starting material	Solvent	Benzo[*b*]fluorenone (% yield)	Benzo[*c*]fluorenone (% yield)	Ratio **9**:**10**
1	**8a**	Benzene	**9e** (61)[b]	**10a** (28)[b]	2.2:1
2	**8a**	Toluene	**9e** (59)[b]	**10a** (23)[b]	2.6:1
3	**8a**	Et_3N	**9a** (100)	–	1:0
4	**8a**	*i*PrOH	**9a** (73)	–	1:0
5	**8a**	CH_3CN	**9a** (15), **9e** (31)	**10a** (1)	15:1
6	**8a**	DMF	**9a** (8), **9e** (15)	–	1:0
7	**8b**	Benzene	**9b**[c]	**10b**[c]	16:1[d]
8	**8c**	Benzene	**9c**[e]	**10c**[e]	2:1[d]
9	**8d**	Benzene	–	–	–
10	**8e**	Benzene	**9e** (70)	–	1:0

[a] All experiments were carried out using freshly distilled solvents and heating at 150°C in a sealed tube overnight.
[b] Yields after desilylation of the crude mixture (**9a**+**10a**).
[c] Inseparable mixture **9b**+**10b**, yield 88%.
[d] By integration of the ^1H NMR signals of the inseparable mixture of regioisomers.
[e] Inseparable mixture **9c**+**10c**, yield 86%.



Scheme 3.

polar aprotic solvents were used, yields were lower (entries 5 and 6) because the starting material became thermally unstable due to partial desilylation. We conclude that aromatic solvents are the most appropriate for obtaining significant yields of **10**.[16]

Summing up, a study of the intramolecular [4+2] cycloaddition of aryldiacetylenes **8** in various solvents shows that in aromatic solvents the major benzo[*b*]fluorenone products of the silyl derivatives **8a** and **8c** are accompanied by significant yields of the corresponding benzo[*c*]fluorenones. This is probably due to the silyl substituted cyclic allene intermediate **11** (R = TMS or TES) isomerizing via a 1,2-dehydro-[10]annulene to the "angular" cyclic allene **14**, which then undergoes aromatization. Unsubstituted and non-silylated derivatives (**8e** and **8b**) gave negligible amounts of rearranged products **10**.

Acknowledgements

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7. Compounds **8** were prepared from *o*-phenylethynylbenzaldehyde (**7**) (obtained in 96% yield by Sonogashira coupling of *o*-bromobenzaldehyde and phenylacetylene)[8] by treatment with the corresponding substituted acetylides followed by oxidation with activated manganese oxide.[9]
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12. Benzo[*c*]fluorenone **10a**: mp 171–172°C (EtOAc–hexane); ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 8.52 (d, $J=9.0$ Hz, 1H), 8.05 (d, $J=7.5$ Hz, 1H), 7.95 (s, 1H), 7.90 (dd, $J=7.5$, 2.3 Hz, 1H), 7.50–7.68 (m, 4H), 7.31 (t, $J=7.5$ Hz, 1H), 0.45 (s, 9H). ^{13}C NMR+DEPT ($CDCl_3$, 62.8 MHz) δ: 195.8 (CO), 145.0 (C), 143.0 (C), 137.0 (CH), 136.7 (C), 135.8 (C), 134.9 (C), 134.8 (CH), 134.0 (C), 129.7 (CH), 129.1 (C), 128.5 (CH), 128.2 (CH), 128.0 (CH), 124.4 (CH), 123.6 (CH), 123.2 (CH), −0.9 ($3\times CH_3$). MS *m*/*z* (rel. intensity%): 302 (M^+, 30), 288 (63), 287 (100), 257 (76); Anal. calcd (%) for $C_{20}H_{18}OSi$: C, 79.42; H, 6.00; found: C, 79.03; H, 6.03.
13. Details of the structure of **10a** and its X-ray crystallographic determination have been deposited at the Cambridge Crystallographic Data Centre as no. CCDC–178032.
14. Rearrangements of arylcarbenes via cyclic allenes have been observed. Xie, Y.; Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1997**, *119*, 1370–1377. See also: Bonvallet, P. A.; McMahon, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 9332–9333.
15. Diagnostic ^{1}H NMR signals to distinguish between benzo[*b*]fluorenones **9** and benzo[*c*]fluorenones **10** are one doublet at 8.4–8.5 ppm (d, $J\approx 8.0$ Hz, H-1) for benzo[*b*]fluoren-11-ones **9** and two doublets at 8.0–8.1 ppm (d, $J\approx 7.5$ Hz, H-1) and 8.5–8.6 ppm (d, $J\approx 8$ Hz, H-8) for benzo[*c*]fluoren-7-ones **10**. See numbering on figures of Scheme 3.
16. In supplementary experiments, various concentrations of **8a** ranging from 20 to 100 mM gave virtually the same ratio of **9** to **10**.