

Domino thermal radical cycloaromatization of non-conjugated aromatic hexa- and heptaynes: synthesis of fluoranthene and benzo[*a*]rubicene skeletons

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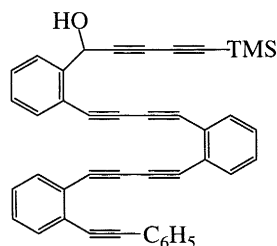
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Abstract

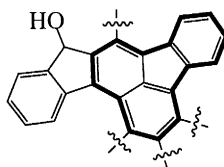
Non-conjugated aromatic hexa- and heptaynes underwent domino thermal radical cycloaromatization at 25°C to yield indenol ring-fused fluoranthene and indenol ring-fused benzo[*a*]rubicene skeletons with helicity. This multi-cyclization reaction proceeded regioselectively to yield [6]helicene derivatives via annulation at the final step. The structure and thermal racemization of [6]helicene derivatives (**6** and **7**) is also described. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: domino thermal radical cycloaromatization; aromatic non-conjugated polyyne; benzo[*a*]rubicene; [6]helicene.

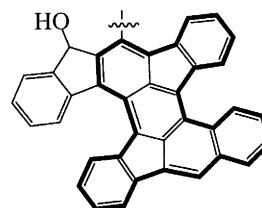
Recently, we reported that the aromatic acyclic tetraynes underwent thermal radical cycloaromatization under mild conditions to yield polycyclic ring systems such as fluorene and fluoreno[3,2-*c*]isochromene skeletons.^{1,2} In the hope of developing this reaction and discovering a new type of polyphenylenes, we planned to study the thermal radical cycloaromatization of aromatic acyclic polyynes. In this paper, we describe domino thermal radical cycloaromatization of hexaynes (**3a–c** and **4a–c**) and heptaynes (**3d** and **4d**) which are converted into indenol ring-fused fluoranthene and indenol ring-fused benzo[*a*]rubicene skeletons with helicity.



Non-conjugated aromatic heptaynes



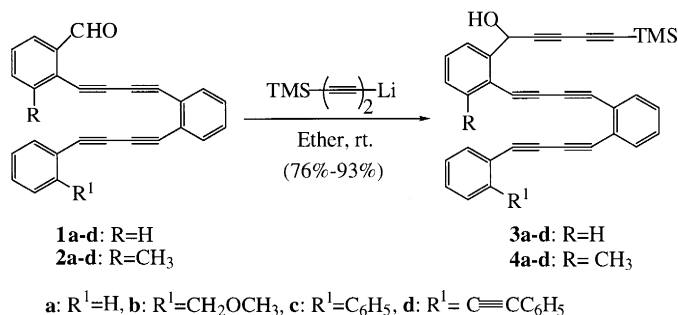
Fluoranthene skeleton



Benzo[*a*]rubicene skeleton

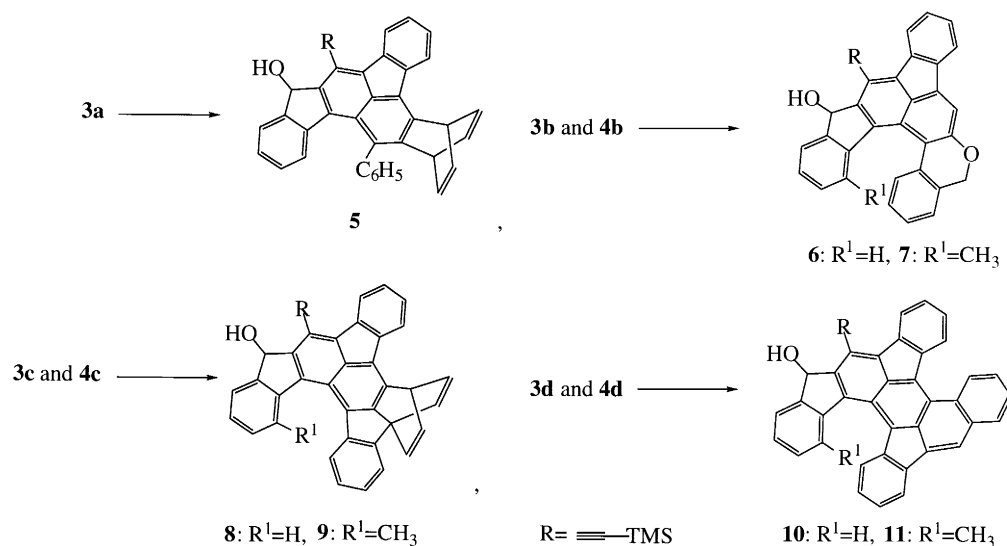
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Polyynes (**3** and **4**) were synthesized from **1** and **2** with 4-trimethylsilylbuta-1,3-diyne-1-yl lithium³ according to the method described in the literature (Scheme 1).^{1,2}



Scheme 1.

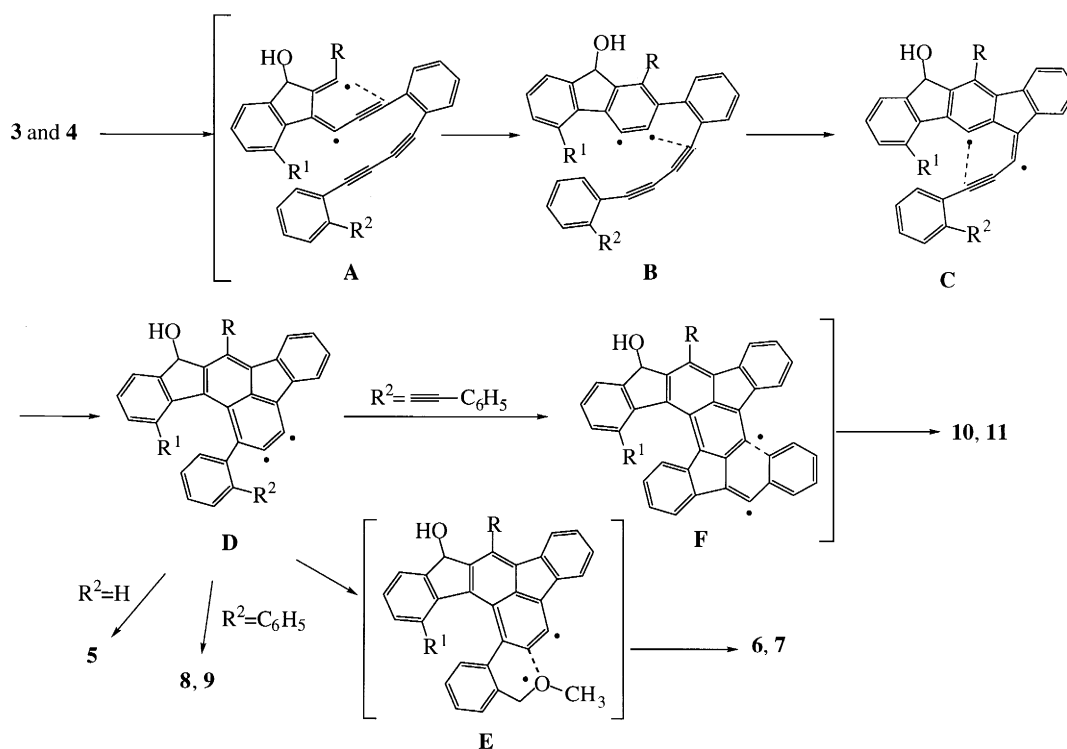
Thermolysis of **3** and **4** in benzene (5 mM) was carried out at 25°C for 72 h in the dark under argon atmosphere (Scheme 2).



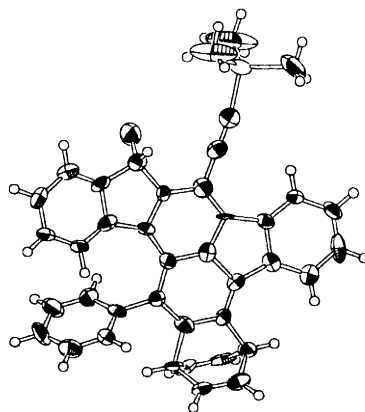
Scheme 2.

Thermolysis of **3a** afforded **5** in 60% yield, which was brought about by an intermolecular Diels–Alder reaction of 1,2-benzyne intermediate (**D**) illustrated in Scheme 3 with benzene used as the solvent. Reaction of **3b** and **4b** under the same conditions afforded **6** and **7** in 20% and 23% yields, respectively, yielding an isochromene skeleton. Treatment of **3c** and **4c** under the same conditions afforded **8** and **9** in 21% and 22% yields, respectively, these results were brought about by an intramolecular Diels–Alder reaction of the 1,2-benzyne intermediate (**D**) with a benzene ring in the parent molecules. On the other hand, **3d** and **4d** underwent the thermal radical cyclization to yield **10** and **11** in 25% and 10% yields, respectively, which had a benzo[*a*]rubicene skeleton in their molecule. The structure of **5** was determined on the basis of spectral data and elementary analysis and finally confirmed by a single crystal X-ray analysis.² The ORTEP drawing of **5** is shown in Fig. 1. The structures of **6–11** were also assigned on the basis of their spectral data and elementary analyses by comparing with the data of **5**.⁴

Compounds (**6–11**) were shown to be a mixture of diastereoisomers because of the helical structures. Among them, compounds (**6**, **7**, **9** and **11**) were separated as two diastereoisomers by silica gel column



Scheme 3.

Fig. 1. The ORTEP drawing of 5^2

chromatography with benzene as an eluent. Thus, the mixture could be distinguished by their ^1H NMR spectral data and R_f -values on TLC (silica gel, eluted with benzene). The isomers with the lower R_f -values, of which two proton signals were observed between δ 5.84 and δ 5.77 ppm for the H^a -hydrogen and between δ 3.21 and δ 2.95 ppm for the H^b -hydrogen of the hydroxy group, were assigned to be in (R^*-M^*)-configurations, while the other isomers with higher R_f -values, of which two proton signals were observed between δ 6.26 and δ 6.14 ppm for the H^a -hydrogen and between δ 3.85 and δ 3.72 ppm for the H^b -hydrogen of the hydroxy group, were assigned to be in (R^*-P^*)-configuration. Fig. 2 shows schematic models of **7** as a typical example. The ^1H NMR spectral data of **7** indicate that the four rings, **A**, **B**, **C** and **D** are arranged in a coplane. The hydrogen atom located on the 5-position of (R^*-P^*)-**7** is

in the axial position and that of (*R**-*M**)-7 is in the equatorial position. In comparison with the chemical shift of the proton of the hydroxy group, the hydroxy group of (*R**-*P**)-7 will be on the coplane with the ethynyl group on the C-ring, while that of (*R**-*M**)-7 will be far from the coplane with the ethynyl group on the C-ring.

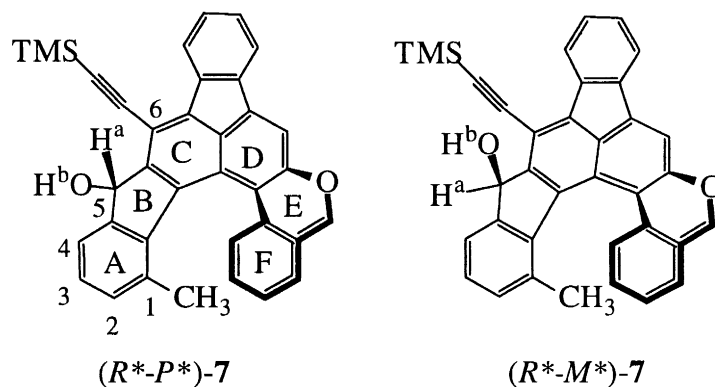


Fig. 2. Schematic models of 7

The thermal racemization of 7 in bromobenzene-*d*₅ using the ¹H NMR method was studied. The inversion rate constant of [(*R**-*P**)-6 and -7] and [(*R**-*M**)-6 and -7] was deduced from the first-order plot which was obtained from the decrease of the peak height of the hydrogen at the 5-position. The rate constant of 6 at 45°C was $k_1=3.7\times10^{-5}\text{s}^{-1}$ for (*R**-*P**)-6 and $k_{-1}=6.8\times10^{-5}\text{s}^{-1}$ for (*R**-*M**)-6, respectively. The half-life time calculated was 110 minutes for (*R**-*P**)-6. The rate constant of 7 at 125°C was $k_1=2.0\times10^{-3}\text{s}^{-1}$ for (*R**-*P**)-7 and $k_{-1}=2.2\times10^{-3}\text{s}^{-1}$ for (*R**-*M**)-7, respectively. The half-life time calculated was 164 minutes for (*R**-*P**)-7. The inversion rate constants indicate that [(*R**-*P**)-6 and -7] are thermodynamically more stable than [(*R**-*M**)-6 and -7]. The difference in the thermal stability between the (*R**-*P**)- and (*R**-*M**)-derivatives may be explained by estimating stereoelectronic interactions between the hydroxy group at the 5-position and the aromatic core. This inversion was not observed by radiation under a 500 W mercury lamp.

A plausible mechanism of the overall transformation for 3 (4) is outlined in Scheme 3. At the first step, 3 (4) gives an outer-ring diradical (A) generated by intramolecular annulation reaction between both buta-1,3-diyne functions of 3 (4). The diradical A is transformed into a fluorenol-1,2-benzyne intermediate (B), one radical of which attacks the terminal carbon of a buta-1,3-diyne moiety, giving an exomethylene radical yielding σ,σ -diradical (C). The diradical (C) is then converted into another 1,2-benzyne intermediate (D) which is the final active intermediate in this transformation. The inter- and intramolecular Diels–Alder reaction of D yield 5, 8 and 9, respectively. The 1,2-benzyne intermediate (D) bearing methoxymethyl group as R² group yields 6 and 7 via a radical intermediate (E), forming active species such as methyl cation, methyl radical and carbene.⁵ The diradical (F), which is formed from D bearing phenylethynyl group as R² group, is converted into benzo[*a*]rubicene derivatives (10 and 11) with helicity.

In conclusion, we have demonstrated a novel method for the preparation of indenol ring-fused fluoranthene and indenol ring-fused benzo[*a*]rubicene skeletons with helicity by domino thermal radical cycloaromatization of non-conjugated aromatic hexa- and heptaynes. This multi-cyclization reaction proceeded regioselectively to yield [6]helicene derivatives through annulation at the final step. The inversion rate constants and half-lives for the racemization of 6 and 7 were also determined.

Acknowledgements

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References

1. Miyawaki, K.; Suzuki, R.; Kawano, T.; Ueda, I. *Tetrahedron Lett.* **1997**, *38*, 3943–3946.
2. Miyawaki, K.; Kawano, T.; Ueda, I. *Tetrahedron Lett.* **1998**, *39*, 6923–6926.
3. Holmes, A. B.; Jennings-White, C. L. D.; Schulthess, A. H. *J. Chem. Soc., Chem. Commun.* **1979**, 840–842.
4. All new compounds gave satisfactory analytical and spectral data. Selected physical data are as follows: (*R**–*P**)-7: Stage orange needles (benzene–hexane), mp 253.3–253.8°C (dec.), R_f =0.43 (benzene), ^1H NMR (CDCl_3 , 400 MHz): 8.37–8.35 (d-like, 1H), 7.83–7.81 (d-like, 1H), 7.63 (s, 1H), 7.53 (d, 1H, J =7.1 Hz), 7.41 (td, 1H, J =7.3, 1.2 Hz), 7.37 (td, 1H, J =7.3, 1.2 Hz), 7.25 (d-like, 1H), 7.22 (td, 2H, J =7.6, 1.5 Hz), 6.97 (td, 1H, J =7.8, 1.2 Hz), 6.92 (d, 1H, J =7.3 Hz), 6.84 (d, 1H, J =7.1 Hz), 6.18 (d, 1H, J =2.9 Hz), 5.35 (d, 1H, J =12.0 Hz), 5.08 (d, 1H, J =12.0 Hz), 3.81 (d, 1H, J =2.9 Hz), 1.74 (s, 3H), 0.45 (s, 9H) ppm. Anal. calcd for $\text{C}_{36}\text{H}_{28}\text{O}_2\text{Si}$: C, 83.04; H, 5.42%. Found: C, 82.93; H, 5.17%. (*R**–*M**)-7: Stage yellow needles (benzene–hexane), mp 252.3–252.8°C (dec.), R_f =0.38 (benzene), ^1H NMR (CDCl_3 , 400 MHz): 8.37 (d, J =7.3 Hz, 1H), 7.82 (d, J =7.1 Hz, 1H), 7.63 (s, 1H), 7.58 (d, 1H, J =7.1 Hz), 7.42–7.35 (m, 2H), 7.26–7.18 (m, 3H), 7.00–6.95 (m, 2H), 6.84 (d, 1H, J =7.6 Hz), 5.83 (d, 1H, J =3.3 Hz), 5.35 (d, 1H, J =12.1 Hz), 5.06 (d, 1H, J =12.1 Hz), 3.21 (d, 1H, J =3.3 Hz), 1.70 (s, 3H), 0.45 (s, 9H) ppm. Anal. calcd for $\text{C}_{36}\text{H}_{28}\text{O}_2\text{Si}$: C, 83.04; H, 5.42%. Found: C, 82.76; H, 5.32%.
5. Ueda, I.; Sakurai, Y.; Kawano, T.; Wada, Y.; Futai, M. *Tetrahedron Lett.* **1999**, *40*, 3919–322.