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

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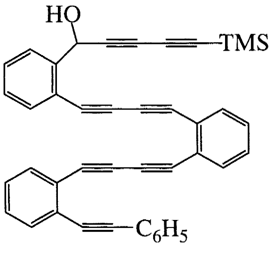
Abstract

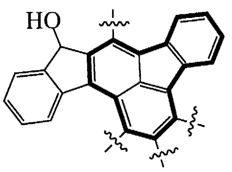
Non-conjugated aromatic hexa- and heptaynes underwent domino thermal radical cycloaromatization at 25°C to yield indenol ring-fused fluoranthene and indenol ring-fused benzo[*a*]rubicene skeletons with helicity. This multi-cyclization reaction proceeded regioselectively to yield [6]helicene derivatives 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.

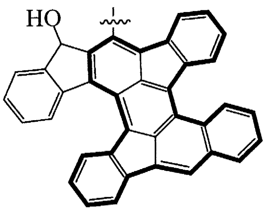
Recently, we reported that the aromatic acyclic tetraynes underwent thermal radical cycloaromatization under mild conditions to yield polycyclic ring systems such as fluorenol and fluoreno[3,2-*c*]isochromenol skeletons.[1,2] In the hope of developing this reaction and discovering a new type of polyphenylenes, 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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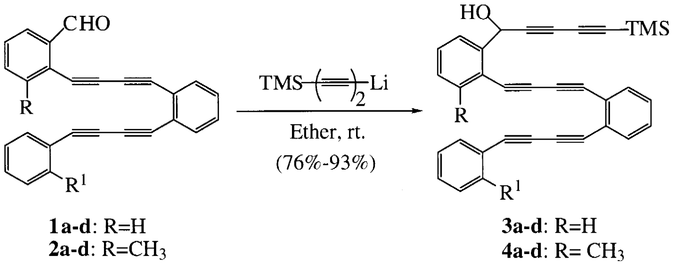
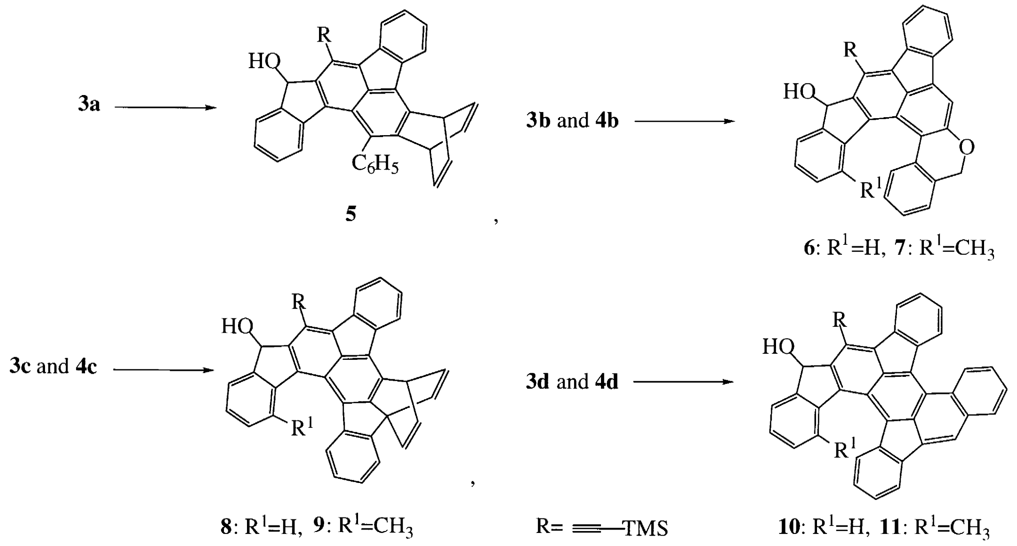
Polyynes (**3** and **4**) were synthesized from **1** and **2** with 4-trimethylsilylbuta-1,3-diyn-1-yl lithium[3] according to the method described in the literature (Scheme 1).[1,2]



a: R^1=H, **b**: R^1=CH_2OCH_3, **c**: R^1=C_6H_5, **d**: R^1= C≡CC_6H_5

Scheme 1.

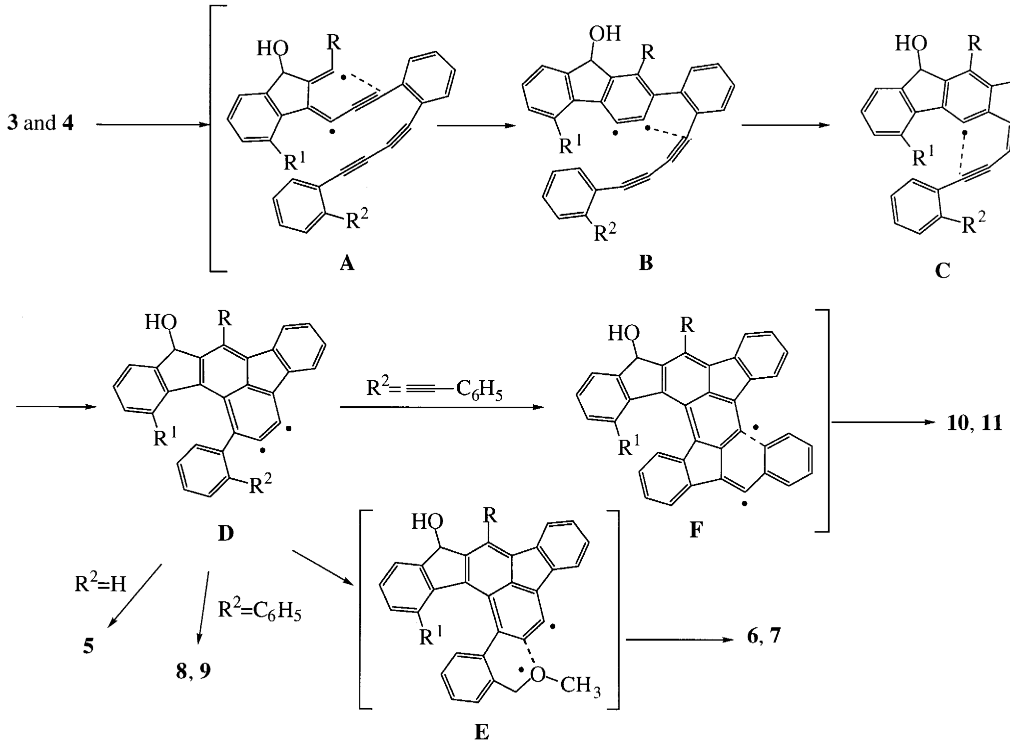
Thermolysis of **3** and **4** in benzene (5 mM) was carried out at 25°C for 72 h in the dark under argon atmosphere (Scheme 2).



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.

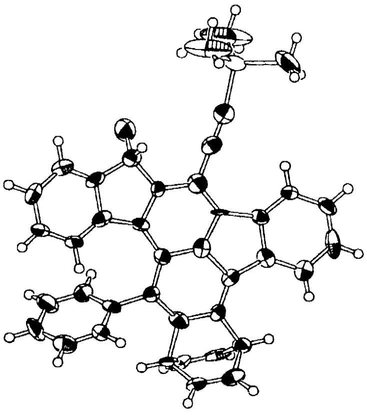
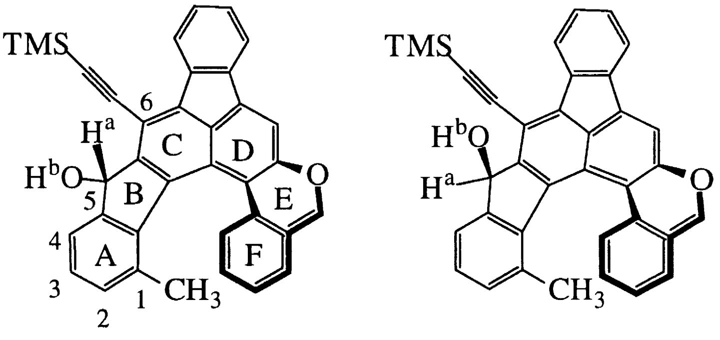


Fig. 1. The ORTEP drawing of **5**[2]

chromatography with benzene as an eluent. Thus, the mixture could be distinguished by their ^{1}H 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 ^{1}H 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.



(*R**-*P**)-**7** (*R**-*M**)-**7**

Fig. 2. Schematic models of **7**

The thermal racemization of **7** in bromobenzene-d_5 using the ^{1}H 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 $k_1=3.7\times10^{-5}s^{-1}$ for (*R**–*P**)-**6** and $k_{-1}=6.8\times10^{-5}s^{-1}$ 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 $k_1=2.0\times10^{-3}s^{-1}$ for (*R**–*P**)-**7** and $k_{-1}=2.2\times10^{-3}s^{-1}$ 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 R^2 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 R^2 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

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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), ^{1}H 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 $C_{36}H_{28}O_2Si$: 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), ^{1}H 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 $C_{36}H_{28}O_2Si$: C, 83.04; H, 5.42%. Found: C, 82.76; H, 5.32%.
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