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### FACILE SYNTHESIS OF HOMOTRIPTYCENES *via* ADDITION OF BENZOCYCLOPROPENE AND ANTHRACENES

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FACILE SYNTHESIS OF HOMOTRIPTYCENES *via*  
ADDITION OF BENZOCYCLOPROPENE AND ANTHRACENES

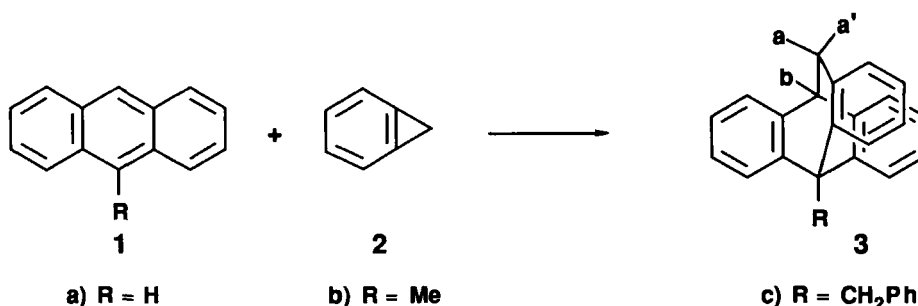
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Triptycene and its homologues have received attention because of their unique structure.<sup>1</sup> However, few examples of homotriptycene (**3a**) have been reported. A synthesis for **3a** and some derivatives by ring-enlargement of 1-aminomethyltriptycene,<sup>2</sup> is lengthy and requires a tedious separation of **3** from the concomitant triptycene isomers. The unique route of Szeimes *et al.*<sup>3</sup> for **3a** using a thermal dehydrogenation of annelated dibenzohomobarrelene [from dibenzo[4.1.1]propellane] is also limited because of the multi-step preparation of the starting propellane and a limited possibility for substituent variations in the homotriptycene skeleton. We now report an alternative method for homotriptycenes using cycloaddition of benzocyclopropene (**2**) to anthracenes (**1**).



Addition of benzocyclopropene to olefins has been increasingly studied mainly from the mechanistic viewpoint.<sup>4</sup> We have used this strained hydrocarbon for the direct construction of the homotriptycenes. The operation is convenient, the starting substances are readily available<sup>5</sup> and the introduction of some substituents is possible. The structure of **3a** was confirmed by the coincidence of its melting point and spectral properties to those of the authentic sample,<sup>2</sup> and the structures of **3b** and **3c** were deduced by satisfactory elemental analyses and the similarity of their spectral properties to those of **3a**. The position of each substituent (R) was assigned on the basis of the coupling constant (4 Hz) between the methylene protons H<sub>a/a'</sub> and the methine proton H<sub>b</sub> in the <sup>1</sup>H NMR spectra.

## EXPERIMENTAL SECTION

**General Procedure. Preparation of 3a.**- A solution of anthracene (**1a**) (70 mg, 0.4 mmol) and benzocyclopropene (**2**)<sup>5</sup> (45 mg, 0.5 mmol) in chloroform (0.5 ml) was heated at 60° for 120 hrs. The reaction mixture was submitted to preparative thin-layer chromatography on silica gel using hexane-benzene 2:1 as a developing solvent to give **3a**, mp. 205°, lit.<sup>2</sup> mp. 205.5° ( $R_f = 0.59$ , 56 mg, 52%).<sup>2</sup> Similar treatment with 9-methyl- and with 9-benzylanthracenes (**1b** and **1c**) yielded the corresponding homotriptycenes (**3b** and **3c**) in 94 and 68% yields respectively.

**3a:** HRMS: 268.1245. Calcd for  $C_{21}H_{16}$ : 268.1250. MS: m/z 268 ( $M^+$ , 100), 267 (53), 265 (21), 253 (22). IR (KBr): 3060, 3020, 2920, 1470  $cm^{-1}$ . UV (MeOH): 271 nm ( $\log \epsilon$  3.23), 264 (3.26), 254 (3.25), 247 (3.26).  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  3.23 (d, 2H,  $H_a$ ,  $H_a$ ,  $J = 4.0$  Hz), 4.23 (t,  $H_b$ ,  $J = 4.0$  Hz), 4.75 (s,  $H_c$ ), 6.63-7.60 (m, 12H).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  36.8, 45.6, 54.7, 124.9, 125.7, 125.9, 126.3, 126.5, 126.8, 128.2, 132.0, 134.2, 140.4, 140.9, 144.0.

**3b:** mp. 198-200°; MS: m/z 282 ( $M^+$ , 53), 267 (100). IR (KBr): 3050, 2920, 1470  $cm^{-1}$ . UV (MeOH): 250 nm ( $\log \epsilon$  2.87), 258 (3.05), 264 (3.19), 270 (3.20), 274 (3.06).  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  2.32 (s, 3H), 3.30 (d, 2H,  $H_a$ ,  $H_a$ ,  $J = 4.0$  Hz), 4.23 (t,  $H_b$ ,  $J = 4.0$  Hz), 6.80-7.50 (m, 12H).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  20.8, 38.5, 44.6, 46.0, 122.4, 125.5, 125.6, 126.2, 126.4, 126.6, 128.2, 132.1, 135.5, 141.0, 143.1, 146.2.

**Anal.** Calcd for  $C_{22}H_{18}$ : C, 93.56; H, 6.44. Found: C, 93.58; H, 6.32

**3c:** mp. 192-193°; MS: m/z 358 ( $M^+$ , 44), 267 (67), 264 (100). IR (KBr): 3020, 2930, 1480  $cm^{-1}$ . UV (MeOH): 259 nm (sh.  $\log \epsilon$  3.20), 264 (3.28), 271 (3.26), 275 (sh. 3.19).  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  3.26 (d, 2H,  $H_a$ ,  $H_a$ ,  $J = 4.0$  Hz), 4.33 (t,  $H_b$ ,  $J = 4.0$  Hz), 4.56 (s, 2H, benzyl methylene), 6.80-7.70 (m, 17H).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  36.4, 39.2, 45.4, 47.0, 122.3, 124.5, 124.9, 125.5, 125.8, 126.1, 126.4, 126.5, 127.4, 130.7, 132.7, 135.4, 137.1, 139.8, 142.9, 143.9.

**Anal.** Calcd for  $C_{28}H_{22}$ : C, 93.81; H, 6.19. Found: C, 93.63; H, 6.09

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