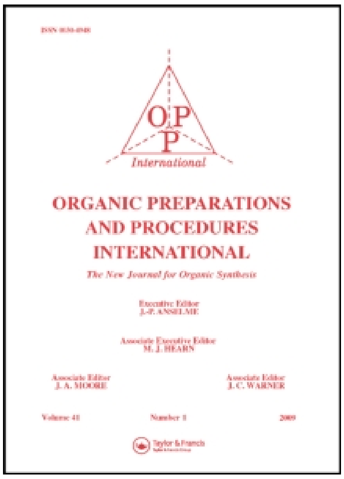

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FACILE SYNTHESIS OF HOMOTRIPTYCENES *via* ADDITION OF BENZOCYCLOPROPENE AND ANTHRACENES

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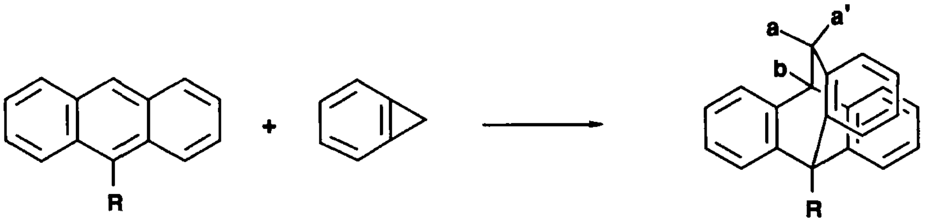
Triptycene and its homologues have received attention because of their unique structure.[1] However, few examples of homotriptycene (3a) have been reported. A synthesis for 3a and some derivatives by ring-enlargement of 1-aminomethyltriptycene,[2] is lengthy and requires a tedious separation of 3 from the concomitant triptycene isomers. The unique route of Szeimes et al.[3] 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).



1 2 3

a) R = H b) R = Me c) R = CH_2Ph

Addition of benzocyclopropene to olefins has been increasingly studied mainly from the mechanistic viewpoint.[4] We have used this strained hydrocarbon for the direct construction of the homotriptycenes. The operation is convenient, the starting substances are readily available[5] 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,[2] 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 $H_{a/a'}$ and the methine proton H_b in the ^1H NMR spectra.

EXPERIMENTAL SECTION

General Procedure. Preparation of 3a.- A solution of anthracene (1a) (70 mg, 0.4 mmol) and benzocyclopropene (2)[5] (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.[2] mp. 205.5° (R_f = 0.59, 56 mg, 52%).[2] 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 ε 3.23), 264 (3.26), 254 (3.25), 247 (3.26). ^1H NMR (200 MHz, $CDCl_3$): δ 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 ($CDCl_3$): δ 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 ε 2.87), 258 (3.05), 264 (3.19), 270 (3.20), 274 (3.06). ^1H NMR (200 MHz, $CDCl_3$): δ 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 ($CDCl_3$): δ 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 ε 3.20), 264 (3.28), 271 (3.26), 275 (sh. 3.19). ^1H NMR (200 MHz, $CDCl_3$): δ 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 ($CDCl_3$): δ 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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