Methyl 8c-Phenyl-4b,8b,8c,8d-tetrahydrodibenzo[a,f]cyclopropa[cd]pentalene-8b-carboxylate

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Methyl Ester/Phenyl Adduct

The preparation of this compound was accomplished by converting phenylacetylenic acid to the corresponding ester, and reacting the ester and anthracene together in a Diels-Alder reaction.

![Chemical Structure]

Preparation of Methyl 9,10-Dihydro-12-phenyl-9,10-ethanoanthracene-11-carboxylate\(^{82}\) (74)

i) Preparation of Methyl 3-Phenyl-2-propynoate\(^{83}\) (76)

The alkyne ester dienophile was prepared by adding 501 mg of 3-phenyl-2-propynoic acid (3.42 mmol), 10 ml of CH\(_2\)Cl\(_2\) and 1 ml of oxaly chloride to a 25 ml round bottom flask and, after the solid had dissolved, refluxing for 2 h. The solvent and excess oxaly chloride were evaporated \textit{in vacuo} to yield an orange oil assumed to be the corresponding acyl chloride. Freshly distilled methanol (15 ml), dried over molecular sieves (4 Å), was added to the flask and the reaction mixture refluxed for 2 h after the cessation of gas evolution. After this time (3 h) the solution was evaporated to dryness, dissolved in diethyl ether and washed with saturated sodium bicarbonate solution and then water. The organic layer was dried, filtered, and concentrated \textit{in vacuo}. The resulting viscous oil was purified by column chromatography (Hexanes/diethyl ether, 96:4) to give the product in 78% yield (386 mg, 2.4 mmol). Spectroscopic data of 76 given below are in complete agreement with the literature values.\(^{83}\)
$^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 7.60-7.20 (5, m, Ar-H), 3.80 (3, s, CO$_2$CH$_3$).

IR (KBr) $v_{\text{max}}$: 2227 (C=C Triple bond), 1708 (C=O), 1436, 1206 cm$^{-1}$.

MS m/e (rel. intensity): 160 (M$^+$, 46.4), 129 (100), 102 (59.4), 75 (41.1).

ii) Diels-Alder Reaction between Anthracene and Methyl 3-Phenyl-2-propynoate

A Carius tube containing 350 mg (2.19 mmol) of methyl 3-phenyl-2-propynoate and 400 mg (2.25 mmol) of anthracene was sealed under vacuum and heated in an oven at 180°C for 6 h. The desired dibenzobarrelene ester product was separated from the resultant brown viscous oil by column chromatography (Hexanes/EtOAc, 97:3), and recrystallized from ethanol to give white prisms (578 mg, 1.71 mmol) in 78% yield. The crystals had a melting point = 154.5-155°C (lit; $^8$2 mp = 153.5-154.5°C) and the spectroscopic data of 74 given below are in complete agreement with the literature values.$^8$2

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 6.98-7.48 (13, m, Ar-H), 5.86 and 5.28 (2, 2s, Bridgehead H$_9$ and H$_{10}$), 3.58 (3, s, CO$_2$CH$_3$).

$^{13}$C NMR (CDCl$_3$, 50 MHz): $\delta$ 166.1 (C=O), 161.1, 145.1, 144.1, 138.4, 136.6 (Vinylc and Ar-C's, No H's); 128.1, 127.8, 127.3, 125.3, 125.0, 123.6, 123.4 (Ar-C-H's); 60.1, 52.1, 51.5 (Bridgehead C's and CO$_2$CH$_3$).

IR (KBr) $v_{\text{max}}$: 1692 (C=O), 1637 (Ph-C=C-E), 1345, 1252 cm$^{-1}$.

MS m/e (rel. intensity): 338 (M$^+$, 25.0), 278 (34.1), 202 (4.6), 178 (100).


Photolysis of Methyl 11-Phenyl-9,10-dihydro-9,10-ethenoanthracene-12-carboxylate (74)

The irradiation of compound 74 was carried out in acetone, benzene, acetonitrile and methanol, rapidly giving rise to a single photoproduct in all cases. Preparative irradiation was performed in a solution of acetone. The reaction could not be monitored by tlc or gc because of the inability to distinguish the starting material from the photoproduct. Reaction progress had to be followed by removing aliquots at 5 minute intervals and running a proton NMR spectrum. In order to avoid difficulties separating the product from the starting material, the reaction mixture was irradiated until no starting material ester peak was observed in the NMR spectrum. After removal of the acetone, a yellow oil was obtained which was purified by column chromatography (PET/EtOAc, 95:5) to give the pure semibullvalene product. Recrystallization from ethanol gave colourless crystals, mp = 150.5-152°C. The photoproduct was identified as:

Methyl 8c-Phenyl-4b,8b,8c,8d-tetrahydroidibenzo[a,f]cyclopropa[cd]
 pentalene-8b-carboxylate (75e)

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.04 (13, m, Ar-H), 4.72 (1, s, Pentalene H$_{4b}$), 4.56 (1, s, Pentalene H$_{8d}$), 3.58 (3, s, CO$_2$CH$_3$).

$^{13}$C NMR (50 MHz, CDCl$_3$): δ 168.9 (C=O); 150.7, 150.5, 136.4, 136.3, 133.9 (Ar-C's, No H's); 128.3, 127.8, 127.6, 127.5, 127.2, 126.8, 125.6, 121.3 (Ar-C-H's); 73.0 (Quaternary pentalene C); 61.9 (Pentalene C-H); 55.7 (Quaternary pentalene C); 51.9, 48.3 (Pentalene C-H and CO$_2$CH$_3$).

IR (KBr) $\nu_{\text{max}}$: 1717 (C=O), 1474, 1224 cm$^{-1}$.

MS m/e (rel. intensity): 338 (M$^+$, 25.2), 279 (79.0), 278 (83.6), 202 (15.9), 178 (31.5), 138.2 (16.2). Calculated mass: 338.1307; found 338.1303.

Analysis calculated for C$_{24}$H$_{18}$O$_2$: C, 85.18; H, 5.36. Found: C, 85.38; H, 5.36.