Cycloaddition reactions of tetracyclones, benzo[b]thiophene S-oxides, and benzo[b]thiophene S,S-dioxides with alkynes

Thies Thiemann
Department of Chemistry, United Arab Emirates University, PO Box 15551, Al Ain, Abu Dhabi, United Arab Emirates
Corresponding Author: Thies Thiemann

Abstract: Tetracyclones have been submitted to Diels-Alder reactions with alkynes to give oligoarylbeneznes. The reactions were performed under diverse conditions, such as in diphenyl ether, under solventless conditions and under microwave irradiation. Also, 3-substituted benzo[b]thiophene S-oxides and benzo[b]thiophene S,S-dioxides have been subjected to [4+2]-cycloaddition reactions with alkynes and alkenes to give aryl substituted extended aromatic systems.

Keywords — tetracyclone,benzo[b]thiophene S-oxide,benzo[b]thiophene S,S-dioxide, thiophene S-oxide, Diels-Alder reaction, cycloaddition, solventless reaction

I. Introduction

Arenes can be synthesized facilely through [4+2]-cycloaddition reactions. The approaches include the reactions of alkynes with cyclic dienes that possess within the ring a function that can be extruded, eg., as CO₂, CO, SO or SO₂. Such cyclic dienes are thiophene S-oxides 1, thiophene S,S-dioxides 2, cyclopentadienones 3 (eg., tetracyclones) and α-pyrones 4, among others (Figure 1). Also, arenoannelated cyclic dienes such as benzo[f]thiophene S-oxides 5 and benzo[b]thiophene S,S-dioxides 6 (Figure 1) belong to this group of reactants that furnish arines in cycloadditions with alkynes, in this case leading to more extended aromatic π-systems. Furthermore, cycloaddition of these reactants with alkenes can lead to aromatic systems upon a subsequent dehydrogenation step, where with certain alkenes such as quinones an externally added oxidant is not always a necessity.

Within this context, tetaarylcylopentadienones (tetracyclones, 7) are commonly used to construct oligoarylbeneznes of considerable complexity, with an easy access to tetra-, penta- and hexaarylbenzenes [1,2]. Molecules with hexaarylbenzene units have been used as sensors [3], as components in organic light emitting diodes (OLEDs) [4] and in molecular switches [5]. A recent comprehensive review of hexaarylbenzenes can be found in ref. 6. We have noted that cycloaddition of tetracyclones at higher temperatures in the presence of air leads to α-pyrones as side products [7]. While α-pyrones lend themselves to cycloaddition reactions with alkynes [8], oftentimes they are less reactive dienes than the cyclopentadienones (tetracyclones). In the following, tetracyclones have been reacted with substituted tolanes (diphenylacetylenes) under diverse reaction conditions such as under solventless conditions, in diphenyl ether as solvent and under microwave irradiation. These reactions are set in juxtaposition and compared with the example of a reaction of a thiophene S-oxide with an alkyne.

In cycloaddition reactions, benzo[b]thiophene S-oxides 5 (R=H) have been found to react as the ene-component in [3+2]-cycloadditions with 1,3-dipoles such as mesitonitrile oxide [9], in Diels-Alder type [4+2]-cycloadditions [10], just as benzo[b]thiophene S,S-dioxides 6 (R=H) [10], and photochemically in [2+2]-cycloadditions [11]. In [4+2]-cycloaddition reactions, benzo[b]thiophene S-oxides 5 (R=H) can act as diene component, also, as is shown by the dimerization of the unsubstituted benzo[b]thiophene S-oxide with itself.
Also, the author has shown previously that certain 2-substituted benzo[\(b\)]thiophene S-oxides can function as dienes in cycloaddition reactions [13]. In the following, the viability of 3-substituted benzo[\(b\)]thiophene S-oxides 5 and 3-substituted benzo[\(b\)]thiophene S,S-dioxides 6 as dienes in \([4+2]\)-cycloaddition with selected alkenes and alkynes is examined.

![Figure 1. Structure of thiophene S-oxide 1, thiophene S,S-dioxide 2, cyclopentadienone 3, \(\alpha\)-pyrone 4, benzo[\(b\)]thiophene S-oxide 5, benzo[\(b\)]thiophene S,S-dioxide 6, tetraarylcyclopentadienone (tetracyclone) 7, and tetraarylthiophene S-oxide 8](image)

II. Experimental

**General.** – Melting points were measured on a Yanaco microscopic hotstage and are uncorrected. Infrared spectra were measured with a JASCO IR-700 and Nippon Denshi JIR-AQ2OM instruments. \(^1\)H and \(^\text{13}\)C NMR spectra were recorded with a JEOL EX-270 spectrometer (\(^1\)H at 270 MHz, \(^\text{13}\)C at 67.8 MHz) and with a JEOL 600 spectrometer (\(^1\)H at 600 MHz, \(^\text{13}\)C at 150.9 MHz). The chemical shifts are relative to TMS (solvent CDCl\(_3\), unless otherwise noted). The assignment of the \(^{\text{13}}\)C-NMR spectra was aided by DEPT experiments (DEPT = distortionless enhancement by polarization transfer), where \((\text{CH}_3)\) denotes methyl, \((\text{CH}_2)\) secondary carbon, \((\text{CH})\) tertiary carbon and \((\text{C}^{\text{quad}})\) a quaternary carbon. Mass spectra were measured with a JMS-01-SG-2 spectrometer. Column chromatography was carried out on Wakogel 300. Elemental analysis was carried out at Kyushu University, Hakozaiki Campus, Fukuoka, Japan. All cycloaddition reactions with tetracyclones were carried out under de-aerated conditions (under argon).

**Chemicals.** – 3-Tetraarylcyclopentadienones were prepared via Weiss reaction (1,3-diarylpropan-2-one 9, substituted benzil 10, benzyltributylammonium hydroxide, dioxane [Scheme 1]) [7,14], \(p,p'\)-Dicyanotolane (17) and 4-(phenylethynyl)benzonitrile (15) [MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 203 (67.4)] were prepared from \(p\)-cyanophenacylactone (10) and \(p\)-bromobenzonitrile (11) and bromobenzene (14), respectively, by Sonogashira coupling reaction (Scheme 2). 3-Ethynylidenbenzo[\(b,d\)]thiophene (20) [MS (EI, 70 eV) m/z (%) 208 (100)] was synthesized by reaction of 3-bromodibenzo[\(b,d\)]thiophene (18) with TMS-acetylene (12) (Sonogashira coupling reaction) with subsequent desilylation (Bu\(_3\)NF, THF) (Scheme 3). \(1\)-n-propyl acetylenedicarboxylate (23) was prepared from acetylenedicarboxylic acid (22) (PrOH, benzene, conc. H\(_2\)SO\(_4\)), while benzyl propiolate (26) was synthesized from propionic acid (24) (benzyl alcohol (25), DMAP, DCC, CH\(_2\)Cl\(_2\)) (Scheme 4). N-4-Iodophenylmaleimide (43) was prepared by reaction of maleic anhydride with 4-iodoaniline (THF) and subsequent cyclization [15]. Benzo[\(b\)]thiophene (27) (TCI) and benzo[\(h\)]thiophen-3-ylboronic acid (31) (TCI) were acquired commercially. 3-(Bromobenzo[\(b\)]thiophene (28) was both acquired commercially and synthesized from benzo[\(b\)]thiophene (27) according to ref. 16. 3-Phenylbenzo[\(b\)]thiophene (30a), 3-(4-methoxyphenyl)benzo[\(b\)]thiophene (30b) and 3-(4-ethoxyphenyl)benzo[\(b\)]thiophene (30c) were prepared from benzil [26] and benzo[\(b\)]thiophene (28) by Suzuki reaction with phenyl, 4-methoxyphenyl, and 4-ethoxyphenylboronic acids (29) (Pd[PPh\(_3\)]\(_2\)Cl\(_2\), PPh\(_3\), Ag, Na\(_2\)CO\(_3\), DME) [for analogous preparation, please see: ref. 17-19]. 3-(4-Acetylphenyl)benzo[\(b\)]thiophene (30d) was prepared by Suzuki reaction between benzo[\(b\)]thiophene (31) and 4-bromocoumarophenone (32) (Pd(PPh\(_3\))\(_3\)Cl\(_2\), PPh\(_3\), Ag, Na\(_2\)CO\(_3\), DME) [for analogous preparation, please see: ref. 20] (Scheme 5). 3-Phenylbenzo[\(b\)]thiophene S-oxide (33) was prepared from 30a analogous to the literature [H\(_2\)O\(_2\), CF\(_3\)CO\(_2\)H, spectroscopic data: IR (KBr) u(1605, 1560, 1086, 1060, 1030, 762, 735, 700 cm\(^{-1}\)); \(^1\)H-NMR (270 MHz, CDCl\(_3\)) \(\delta 7.01\) (1H, s), 7.50 – 7.56 (8H, m), 8.00 – 8.02 (1H, m); \(^\text{13}\)C-NMR (67.8 MHz, CDCl\(_3\)) \(\delta 124.4, 126.6, 128.0\) (2C), 129.0 (2C), 129.9, 131.7, 132.5, 132.6, 137.2, 146.5, 148.5; ref. 21,22] (Scheme 6). 3-(4-Methoxyphenyl)benzo[\(b\)]thiophene S,S-dioxide (35a) [20, 3-(4-
ethoxyphenyl)benzo[b]thiophene S,S-dioxide (35b), 3-bromobenzo[b]thiophene S,S-dioxide (34b) [23], 4-acetylphenylbenzo[b]thiophene S,S-dioxide (35c) and 3-phenylbenzo[b]thiophene S,S-dioxide (35d) were prepared by oxidation of the corresponding benzo[b]thiophenes (m-CPBA, CH₂Cl₂) (Scheme 7).

4-(Phenethylnyl)benzamid (16). – To 15 (850 mg, 4.2 mmol) and tetrabutylammonium hydrogenosulfate (Bu₄NHSO₄, 1.0 g) in CH₂Cl₂ (45 mL) were added 30% w%aq. H₂O₂ (10 mL) and a 20% w%aq. NaOH solution (10 mL), and the resulting reaction mixture was stirred for 12h at rt. Thereafter, it was poured into water (20 mL) and extracted with CHCl₃. The organic phase was dried over anhydrous MgSO₄ and concentrated in vacuo. The residue was subjected to column chromatography on silica gel (CHCl₃-ethyl acetate: 9:1) to give 16 (500 mg, 54%) as a colorless solid, mp. 250 °C [24]. 1H-NMR (270 MHz, CDCl₃) δ 5.80 – 6.15 (2H, bs, NH₂), 7.35 – 7.38 (3H, m), 7.53 – 7.57 (2H, m), 7.60 (2H, d, 3J = 8.4 Hz), 7.79 (2H, d, 3J = 8.4 Hz). 13C-NMR (67.8 MHz, CDCl₃) δ 127.6 (2C, CH), 129.9 (2C, CH), 130.2 (2C, CH), 130.9 (C quat), 169.1 (C=O).

3-Ethynylidibenzo[b,d]thiophene S,S-dioxide (21) To 3-ethynylidibenzo[b,d]thiophene (20, 165 mg, 0.79 mmol) in CH₂Cl₂ (5 mL) was added at 0 °C mp-PBA (550 mg, 70%, 2.23 mmol) as a colorless solid. Thereafter, the suspension was stirred at rt for 12h. The reaction mixture was poured in aq. Na₂CO₃ (5 w%, 15 mL) and extracted with CH₂Cl₂ (3 X 15 mL). The organic phase was dried over anhydrous MgSO₄ and concentrated in vacuo. The residue was subjected to column chromatography on silica gel (CHCl₃/ether 7:1) to give 21 (147 mg, 77%) as a colorless solid; mp. 252 °C; 1H-NMR (270 MHz, CDCl₃) δ 3.31 (1H, s, C=CH), 7.53-7.69 (3H, m), 7.77-7.85 (4H, m), 7.88 (1H, s); 13C-NMR (67.8 MHz, CDCl₃) δ 81.8 (C=CH₂), 81.8 (C=CH₂), 121.7 (CH), 122.2 (CH), 122.3 (CH), 125.0 (CH), 128.1 (C quat), 130.8 (CH), 131.9 (C quat), 133.9 (CH), 134.0 (CH), 137.5 (C quat), 137.9 (C quat); MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 241 (MH⁺, 9.4).

1-(4-Cyanophenyl)-2,3,4,5-tetraphenylbenzene (36a). – A mixture of tetracyclone (7a, 216 mg, 0.59 mmol) and 4-cyanophenylacetylene (13, 150 mg, 1.18 mmol) was heated at 175 °C for 5 min. Thereafter, the excess 4-cyanophenylacetylene is sublimated off and the remaining mass is taken up in hexane/ether (10:1) to give 36a (255 mg, 90%) as a colorless solid, mp. 203 °C; 1H-NMR (270 MHz, CDCl₃) δ 6.75 – 6.97 (16H, m), 7.15 (4H, m), 7.25 (2H, d, 3J = 8.6 Hz), 7.44 (2H, d, 3J = 8.6 Hz), 7.51 (1H, s); 13C-NMR (67.8 MHz, CDCl₃) δ 110.0 (C quat), 118.9 (C quat), 125.5 (CH), 126.1 (CH), 126.5 (CH), 126.7 (2C, CH), 127.0 (2C, CH), 127.2 (2C, CH), 127.7 (2C, CH), 129.8 (2C, CH), 130.2 (2C, CH), 130.6 (2C, CH), 130.9 (CH), 131.3 (2C, CH), 131.4 (2C, CH), 131.6 (5) 138.9 (Cquat), 139.2 (2C, Cquat), 139.5 (Cquat), 139.8 (Cquat), 140.4 (Cquat), 141.2 (Cquat), 141.3 (Cquat), 142.1 (Cquat), 146.7 (C quat).

1-(4- Carboxamidophenyl)-2,3,4,5-tetraphenylbenzene (37a). – To 36a (285 mg, 0.59 mmol) and tetrabutylammonium hydrogenosulfate (Bu₄NHSO₄, 150 mg) in CH₂Cl₂ (10 mL) were added 30% w%aq. H₂O₂ (2 mL) and a 20% w%aq. NaOH solution (2 mL), and the resulting reaction mixture was stirred for 12h at rt. Thereafter, it was poured into water (20 mL) and extracted with CHCl₃. The organic phase was dried over anhydrous MgSO₄ and concentrated in vacuo. The residue was subjected to column chromatography on silica gel (CHCl₃-ethyl acetate: 9:1) to give 37a (257 mg, 87%) as a colorless solid; 1H-NMR (270 MHz, CDCl₃) δ 7.50 – 6.00 (2H, bs, NH₂), 6.76 – 6.94 (15H, m), 7.16 (5H, bs), 7.24 (2H, d, 3J = 8.4 Hz), 7.55 (1H, s), 7.62 (2H, d, 3J = 8.4 Hz); 13C-NMR (67.8 MHz, CDCl₃) δ 125.4 (CH), 125.7 (CH), 125.9 (CH), 126.4 (CH), 126.7 (2C, CH), 126.7 (2C, CH), 127.1 (2C, CH), 127.6 (2C, CH), 129.9 (2C, CH), 130.2 (2C, CH), 130.9 (Cquat), 131.1 (CH), 131.4 (2C, CH), 131.4 (2C, CH), 131.5 (4C, CH), 139.2 (5) (Cquat), 139.5 (2C, Cquat), 139.7 (Cquat), 139.9 (5) (Cquat), 140.0 (Cquat), 141.0 (Cquat), 141.5 (Cquat), 142.0 (Cquat), 145.7 (Cquat), 169.1 (Cquat, C=O N).
C, CH₃), 127.0 (4C, CH), 127.1 (5) (4C, CH), 130.5 (2C, CH), 131.0 (5) (2C, CH), 131.1 (CH), 132.6 (4C, CH, \( J_{CF} = 7.8 \) Hz), 135.9 (C\text{quat}, \( J_{CF} = 3.9 \) Hz), 136.0(5) (C\text{quat}, \( J_{CF} = 3.9 \) Hz), 138.8 (C\text{quat}), 139.5(5) (C\text{quat}), 139.6 (C\text{quat}), 139.7 (C\text{quat}), 139.8 (C\text{quat}), 140.1(5) (C\text{quat}), 140.2(6) (C\text{quat}), 140.3 (C\text{quat}), 140.9 (C\text{quat}), 145.9 (2C, C\text{quat}), 160.7 (2C, C\text{quat}, \( J_{CF} = 244.3 \) Hz).

4-(4-Carboxamidomethyl)-1,2-bis(4-fluorophenyl)-3,5,6-triphenylbenzene (37b). – 36b (450 mg, 0.76 mmol) and tetraethylammonium hydrogensulfate (Bu₄NHSO₄, 195 mg) in CH₂Cl₂ (12 mL) were added 30% \( \text{aq. H}_{2}O \) (2.6 mL) and a 20% \( \text{aq. NaOH} \) solution (2.6 mL), and the resulting reaction mixture was stirred for 12 h at rt. The mixture was then poured into water (20 mL) and extracted with CHCl₃. The organic phase was dried over anhydrous MgSO₄ and concentrated in vacuo. The residue was subjected to column chromatography on silica gel (CHCl₃-ethyl acetate: 9:1) to give 37b (340 mg, 73%) as a colorless solid, mp. 345 °C. \(^1\)H-NMR (270 MHz, CDCl₃) \( \delta \) 6.75 – 7.14 (2H, m, \( J = 8.1 \) Hz), 7.18 (4H, d, \( J = 8.1 \) Hz), \(^1^\text{C}-\text{NMR} \) (67.8 MHz, CDCl₃) \( \delta \) 109.4 (C\text{quat}, 2C, CN), 113.8 (C\text{quat}, 2C), 125.3 (2C, CH), 125.6 (2C, CH), 126.4 (4C, CH), 126.7 (4C, CH), 130.5 (4C, CH), 130.7 (4C, CH), 130.7(5) (4C, CH), 137.7 (2C, C\text{quat}), 138.9 (2C, C\text{quat}), 139.3 (2C, C\text{quat}), 140.0 (2C, C\text{quat}), 141.3 (2C, C\text{quat}), 144.9 (2C, C\text{quat}); MS (EI) \( m/z \) (%) 585 (M+1, 11.2), 584 (M, 114). HRMS Found: 584.2234. Calcul. for C₃₁H₂₄NO₂F₅; 584.2252.

1,2-Bis(4-cyanophenyl)-3,4,5,6-tetraphenylbenzene (36c). – A mixture of p,p'-dicyanotoluene (17, 228 mg, 1.0 mmol) and tetracyclone (7a, 192 mg, 0.5 mmol) in diphenylether (1.1 mL) was heated at 175 °C for 24 h. The cooled solution was subjected to column chromatography on silica gel (hexane – hexane/ether: 10/1) to give 36d (280 mg, 85%) as a colorless solid; \(^1\)H-NMR (270 MHz, CDCl₃) \( \delta \) 7.14 (2H, d, \( J = 8.6 \) Hz). \(^1^\text{C}-\text{NMR} \) (67.8 MHz, CDCl₃) \( \delta \) 108.9(5) (C\text{quat}, 119.1 (C\text{quat}, CN). 126.7 (5C, CH), 126.9 (4C, CH), 131.2 (6C, CH), 131.2(5) (6C, CH), 138.5 (C\text{quat}), 139.8 (2C, C\text{quat}), 139.9 (2C, C\text{quat}, 140.0(5) (2C, C\text{quat}), 140.2 (C\text{quat}), 140.6(5) (2C, C\text{quat}), 141.3 (C\text{quat}), 146.2 (C\text{quat}); MS (FAB, 3-nitrobenzyl alcohol) \( m/z \) (%) 559 (M+, 100). HRMS Found: 559.2296. Calcul. for C₃₁H₂₄N₂O₂: 559.2300. 36d (250 mg, 0.45 mmol) and tetrabutyrammonium hydrogensulfate (Bu₄NHSO₄, 115 mg) in CH₂Cl₂ (10 mL) were added 30% \( \text{aq. H}_{2}O \) (2.0 mL) and a 20% \( \text{aq. NaOH} \) solution (2.0 mL), and the resulting reaction mixture was stirred for 12 h at rt. Thereafter, it was poured into water (20 mL) and extracted with CHCl₃. The organic phase was dried over anhydrous MgSO₄ and concentrated in vacuo. The residue was subjected to column chromatography on silica gel (CHCl₃-ethyl acetate: 9:1) to give 37e (185 mg, 71%) as a colorless solid, MS (FAB, 3-nitrobenzyl alcohol) \( m/z \) (%) 578 (MH⁺, 1.2); 559 (M, 2.4). HRMS Found: 578.2487. Calcul. for C₃₁H₂₄N₂O₂: 578.2438.

1,2-Bis(4-methoxyphenyl)-3,4,5,6-tetraphenylbenzene (36e). – A solventless mixture of 4,4'-dimethoxytolane (38a, 171 mg, 0.72 mmol) and tetracyclone (7a, 138 mg, 0.36 mmol) was heated at 175 °C for 18 h. The cooled mixture was subjected to column chromatography on silica gel (hexane–hexane/ether: 2:1) to give 36e (189 mg, 88%) as a colorless solid, mp. 292 °C (Lit. 292 – 293 °C [1]); \(^1\)H-NMR (270 MHz, CDCl₃) \( \delta \) 3.59 (6H, s, 2 OCH₃), 6.41 (4H, d, \( J = 8.9 \) Hz), 7.14 (2H, d, \( J = 8.6 \) Hz). \(^1^\text{C}-\text{NMR} \) (67.8 MHz, CDCl₃) \( \delta \) 54.9 (2C, OCH₃), 112.2 (4C, CH), 125.0(5) (2C, CH), 125.1 (2C, CH), 126.5 (4C, CH), 126.6 (4C, CH), 131.4 (8C, CH), 132.4 (4C, CH), 133.2 (2C, C\text{quat}), 140.1 (2C, C\text{quat}), 140.6 (2C, C\text{quat}), 140.8 (2C, C\text{quat}), 140.9 (2C, C\text{quat}), 156.9 (2C, C\text{quat}); MS (FAB, 3-nitrobenzyl alcohol) \( m/z \) (%) 595 (M+1, 5.9), 594 (M, 7.6). HRMS Found: 594.2554. Calcul. for C₃₃H₂₄O₂: 594.2559 (FAB).

1,2-Bis(p-toly)-3,4,5,6-tetraphenylbenzene (36f). – A mixture of bis(p-tolyacetyle) (38b, 589 mg, 2.86 mmol) and tetracyclone (7a, 220 mg, 0.57 mmol) was heated at 175 °C for 3 h. Thereafter, the cooled solution was subjected to column chromatography (CH₃Cl₂ – hexane 1:1) to give 36f as a solid (292 mg, 91%), mp. 355°C (Lit. 357 – 358 °C [1]); \(^1\)H-NMR (270 MHz, CDCl₃) \( \delta \) 2.32 (6H, s, 2 CH₂), 6.65 (4H, d, \( J = 8.1 \) Hz), 6.69 (4H, d, \( J = 8.1 \) Hz), 6.82 (20H, m); \(^1^\text{C}-\text{NMR} \) (67.8 MHz, CDCl₃) \( \delta \) 210.0 (2C, CH₂), 125.0 (2C, CH), 125.0(5) (2C, CH), 126.5 (8C, CH), 127.3 (4C, CH), 131.2(5) (4C, CH), 131.4(5) (8C, CH), 134.3 (2C, C\text{quat}).

DOI: 10.9790/5736-1204012442 www.iosrjournals.org 27 [Page]
1-(Dibenzo[b,d]thien-3-yl)-2,3,4,5-tetraphenylbenzene (36g) and 1-(1,1-dioxo-dibenzo[b,d]thien-3-yl)-2,3,4,5-tetraphenylbenzene (37d). — A mixture of 3-ethyldibenzo[b,d]thiophene (20, 104 mg, 0.5 mmol) and tetracyclone (7a, 192 mg, 0.5 mmol) in diphenylether (1.5 mL) was heated at 175 °C for 30 min. Thereafter, the cooled solution was subjected to column chromatographic separation on silica gel (hexane → hexane/toluene 3:1) to give 36g (180 mg, 64%) as colorless solid, mp. 237 °C; 1H-NMR (270 MHz, CDCl3) δ 6.70 − 6.95 (14H, m), 7.15 − 7.25 (7H, m), 7.39 − 7.41 (2H, m), 7.57 (1H, d, J = 7.0 Hz), 7.69 (1H, s), 7.77 − 7.83 (1H, m), 7.93 − 7.96 (1H, m), 8.02 (d, 1H, J = 1.6 Hz). To a solution of 36g (222 mg, 0.31 mmol) in CH2Cl2 (5 mL) was added m-CPBA (215 mg, 0.87 mmol). The resulting mixture was stirred for rt for 12h. The reaction mixture was poured inaq. Na2CO3 (5 w%, 15 mL) and extracted with CH2Cl2 (3 X 15 mL). The organic phase was dried over anhydrous MgSO4 and concentrated in vacuo. The residue was subjected to column chromatography on silica gel (CH2Cl2/ether 7:1) to give 37d (210 mg, 91%) as a pale yellow solid, mp. > 250 °C; 1H-NMR (270 MHz, CDCl3) δ 3.83 − 5.01 (10H, m), 6.71 − 7.94 (14H, m), 7.39 − 8.03 (7H, m), 8.17 (1H, d, J = 1.6 Hz).}

2°,3°-Bis(4-fluorophenyl)-5°-(4-cyanophenyl)-p-quinquephenyl (36h). — A mixture of 2,5-bis(p-biphenylicyclopentadiene (7e, 58 mg, 0.10 mmol) and 4-cyanotolane (13, 50 mg, 0.39 mmol) in diphenylether (150 mg) has been heated at 175 °C for 10h. The cooled mixture was subjected to column chromatography on silica gel (hexane → hexane/ether/CHCl3 1:1:1) to give 36h (54 mg, 81%) as a colorless solid, mp. 300 °C; 1H-NMR (270 MHz, CDCl3) δ 1.40 − 2.35 (20H, m), 3.21 − 3.51 (3H, m), 7.19 (2H, d, J = 6.1 Hz), 7.35 − 7.47 (12H, m), 8.20 (2H, d, J = 8.0 Hz), 8.52 (2H, d, J = 8.1 Hz), 8.70 − 8.75 (4H, m), 8.83 (1H, d, J = 8.0 Hz), 8.93 (1H, d, J = 8.0 Hz), 9.10 (1H, d, J = 8.0 Hz).}

1-Phenylethynyl)-2,3,4,5,6-pentaphenylbenzene (36i). — A mixture of tetracyclone (7a, 123 mg, 0.33 mmol) and diphenylethylene (38c, 258 mg, 1.28 mmol) was heated for 3h at 150 °C. The reaction mixture was directly crystallized and recrystallized from ether/hexane 1:1 to yield 36i (175 mg, 94%) as a colorless solid, mp. 283 °C; 1H-NMR (270 MHz, CDCl3) δ 1.40 − 2.35 (20H, m), 3.21 − 3.51 (3H, m), 7.19 (2H, d, J = 6.1 Hz), 7.35 − 7.47 (12H, m), 8.20 (2H, d, J = 6.1 Hz), 8.52 (2H, d, J = 6.1 Hz); 13C-NMR (67.8 MHz, CDCl3) δ 1.40 − 2.35 (20H, m), 3.21 − 3.51 (3H, m), 7.19 (2H, d, J = 6.1 Hz), 7.35 − 7.47 (12H, m), 8.20 (2H, d, J = 6.1 Hz), 8.52 (2H, d, J = 6.1 Hz); 13C-NMR (67.8 MHz, CDCl3) δ 1.40 − 2.35 (20H, m), 3.21 − 3.51 (3H, m), 7.19 (2H, d, J = 6.1 Hz), 7.35 − 7.47 (12H, m), 8.20 (2H, d, J = 6.1 Hz), 8.52 (2H, d, J = 6.1 Hz).}

1-Phenylethynyl)-2,3,4,5,6-pentaphenylbenzene (36i). — A mixture of 3,4-bis(4-fluorophenyl)-2,5-diphenylcyclopentadienone (7b, 378 mg, 0.99 mmol) and bis-(4-cyanophenyl)acetylene (17, 198 mg, 0.99 mmol) was heated at 175 °C for 12h. The cooled mixture was subjected to column chromatography on silica gel (hexane → CHCl3 1:1) to give 36j (475 mg, 85%) as colorless plates, mp. 380 °C; 1H-NMR (270 MHz, CDCl3) δ 6.59 (4H, dd, J = 8.1 Hz, J = 8.1 Hz), 6.71 − 6.77 (26H, m), 7.52 (2H, d, J = 7.6 Hz), 13C-NMR (67.8 MHz, CDCl3) δ 88.9 (4C), 96.9 (s=C), 125.4 (2C, C qua), 125.5 (2C, CH), 126.3 (2C, CH), 126.6 (2C, CH), 126.7 (4C, CH), 127.0 (4C, CH), 127.6 (2C, C qua), 127.9 (2C, CH), 128.4 (CH), 130.9 (4C, CH), 131.1 (2C, CH), 131.2 (2C, CH), 131.3 (4C, CH), 132.5 (CH), 139.9 (2C, C qua), 140.2 (C qua), 140.5 (2C, C qua), 141.2 (C qua), 143.2 (C qua). MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 558 (M+, 81), 559 (M+1, 4.8). HRMS: Found: 558.2342. Calcd. for C21H15N2F2: 558.2348.

4.5-Bis-(4-cyanophenyl)-1,2-bis-(4-fluorophenyl)-3,6-diphenylbenzene (36k). — A solventless mixture of 3,4-bis-(4-fluorophenyl)-2,5-diphenylcyclopentadienone (7b, 483 mg, 1.16 mmol) and p,p′-dimethoxytolane (38a, 600 mg, 2.52 mmol) was heated at 175 °C for 23h. The cooled mixture is subjected to column chromatography on silica gel (hexane/CHCl3/ether 10:1:1) to give 36k (690 mg, 94%) as a colorless solid; 1H-NMR (67.8 MHz, CDCl3): δ 3.83 − 5.01 (10H, m), 3.21 − 3.51 (3H, m), 7.19 (2H, d, J = 6.1 Hz), 7.35 − 7.47 (12H, m), 8.20 (2H, d, J = 6.1 Hz), 8.52 (2H, d, J = 6.1 Hz).
NMR (270 MHz, CDCl₃) δ : 13C-NMR (67.8 MHz, CDCl₃) δ 54.9 (2C, OCH₃), 112.2 (4C, CH), 113.7 (2C, Cquat, JCF = 21.2 Hz), 125.2 (2C), 126.8 (4C, CH), 131.3 (4C, CH), 132.3 (2C, CH), 132.7 (4C, CH, JCF = 7.9 Hz), 132.9 (Cquat), 136.6 (2C, Cquat, JCF = 4.5 Hz), 139.2 (Cquat), 140.5 (Cquat), 140.6 (Cquat), 140.8 (Cquat), 157.0 (Cquat), 160.6 (2C, Cquat, JCF = 242.6 Hz); MS (70 eV) m/z (%): 630 (M⁺, 100). HRMS Found: 630.2378. Calcd. for C₃₂H₂₀O₂F₂: 630.2370.

4,5-Bis-(4-nitrophenyl)-1,2-bis-(4-fluorophenyl)-3,6-diphenylbenzene (36L). A mixture of 3,4-bis(4-fluorophenyl)-2,5-diphenylcyclopentadiene (7b, 142 mg, 0.34 mmol) and p,p′-dinitrotoluene (38d, 64 mg, 0.225 mmol) in diphenyl ether (500 mg) was heated to 175 °C for 10h. The cooled mixture was subjected to column chromatography on silica gel (hexane → hexane/CHCl₃/ether 5:1:1) to give 36L (94 mg, 63%) colorless solid; mp: 340 °C. 1H-NMR (270 MHz, CDCl₃) δ 6.61 (4H, d, J = 8.6 Hz, 6.73 – 6.79 (8H, m), 6.90 – 6.93 (6H, m), 6.99 (4H, d, J = 8.6 Hz); 13C-NMR (67.8 MHz, CDCl₃) δ 141.1 (4C, CH, JCF = 21.2 Hz), 122.4 (4C, CH), 126.4 (2C, CH), 127.4 (4C, CH), 130.9 (4C, CH), 131.9 (4C, CH), 132.4 (5C, CH, JCF = 8.4 Hz), 135.4 (2C, Cquat, JCF = 3.9 Hz), 138.9 (2C, Cquat), 140.7 (2C, Cquat), 140.9 (2C, Cquat), 145.8 (2C, Cquat), 147.0 (2C, Cquat), 161.7 (2C, Cquat, JCF = 245.9 Hz).

1-(4-Cyanophenyl)-3,4-bis-(4-fluorophenyl)-2,5-diphenylbenzene (36m). A mixture of 3,4-bis(4-fluorophenyl)-2,5-diphenylcyclopentadiene (7b, 420 mg, 1.00 mmol) and 4-cyanophenylacetylene (13, 128 mg, 1.00 mmol) was heated to 175 °C for 9h.* The cooled mixture was subjected to column chromatography on silica gel (hexane – ethane – CH₂Cl₂ 10:1:1) to give 36m (390 mg, 75%) as a colorless solid, mp: 300 °C. 1H-NMR (270 MHz, CDCl₃) δ 6.60 – 6.81 (9H, m), 6.97 – 6.99 (6H, m), 7.18 – 7.20 (6H, m), 7.24 (2H, d, J = 8.1 Hz), 7.44 (2H, d, J = 8.1 Hz), 7.51 (1H, s); 13C-NMR (67.8 MHz, CDCl₃) δ 110.2 (Cquat), 118.4 (2C, CH, JCF = 21.2 Hz), 114.3 (2C, CH, JCF = 21.2 Hz), 118.8 (Cquat, CH), 126.3 (CH), 126.7 (CH), 127.4(5C, CH), 127.8(5C, CH), 129.8 (2C, CH), 131.1 (CH), 131.2 (2C, CH), 131.5 (2C, CH), 132.7 (2C, CH, JCF = 7.7 Hz), 132.8 (2C, CH, JCF = 7.9 Hz), 135.4 (Cquat, JCF = 3.4 Hz), 135.6 (Cquat, JCF = 3.9 Hz), 138.9(5C, Cquat), 139.2 (Cquat), 139.5 (Cquat), 140.9 (Cquat), 141.1(5C, Cquat), 141.4 (Cquat), 146.4 (2C, Cquat); MS (FAB, 3-nitrobenzyl alcohol) m/z (%): 519 (M⁺) (100). HRMS Found: 519.1799. Calcd. for C₃₈H₂₇F₂N₂: 519.1799. *Care has to be taken to heat the reaction vessel completely as 4-cyanophenylacetylene sublimates under the conditions.

1,2-Bis-(4-fluorophenyl)-3,6-diphenyl-4,5-bis-(p-toly)benzene (36o). A solution of 3,4-bis-(4-fluorophenyl)-2,5-diphenylcyclopentadiene (7b, 274 mg, 0.65 mmol) and phenylacetylene (38e, 663 mg, 6.5 mg) was heated at 175 °C for 3 min. The cooled mixture was taken up in hexane-ether (9:1) to give 36o (310 mg, 97%) as a colorless oil; mp: 233 °C. 1H-NMR (270 MHz, CDCl₃) δ 6.55 – 6.96 (15H, m), 7.14 – 7.18 (8H, bs), 7.56 (1H, s); 13C-NMR (67.8 MHz, CDCl₃) δ 113.6 (2C, CH, JCF = 21.2 Hz), 113.9 (2C, CH, JCF = 21.2 Hz), 125.5 (CH), 126.1 (CH), 126.2 (CH), 126.8 (2C, CH), 127.4 (2C, CH), 127.5 (2C, CH), 126.9 (4C, CH), 131.1 (2C, CH), 131.3 (CH), 132.5 (2C, CH, JCF = 8.0 Hz), 132.6 (2C, CH, JCF = 6.7 Hz), 131.3 (CH), 134.4 (Cquat), 135.5 (Cquat, JCF = 3.4 Hz), 135.9 (Cquat, JCF = 1.6 Hz), 138.1 (Cquat), 139.2 (Cquat), 140.5 (Cquat), 140.7 (Cquat), 140.8 (Cquat), 141.1 (Cquat), 141.2 (Cquat), 162.0 (2C, Cquat, JCF = 246.0 Hz); MS (FAB, 3-nitrobenzyl alcohol) m/z (%): 494 (M⁺, 100). HRMS Found: 494.1853. Calcd. for C₃₉H₂₉F₂: 496.1846 (FAB).

1,2-Bis-(4-bromophenyl)-3,4,5,6-tetraphenylbenzene (36p). A solution of p,p′-dibromotoluene (38f, 81 mg, 0.24 mmol) and tetracyclone (7a, 92 mg, 0.24 mmol) in diphenyl ether (0.3 mL) was heated at 175 °C for 36h.* Column chromatography on silica gel (hexane → hexane/toluene 1:1) gave 36p (140 mg, 85%) as a colorless solid; mp: 350 °C. 1H-NMR (270 MHz, CDCl₃) δ 6.68 (4H, d, J = 8.6 Hz), 6.77 – 6.89 (20H, m), 7.02 (4H, d, J = 8.6 Hz); 13C-NMR (67.8 MHz, CDCl₃) δ 119.7 (2C, Cquat), 125.3 (2C, CH), 125.5 (2C, CH), 126.6 (4C, CH), 126.8 (4C, CH), 130.0 (4C, CH), 131.2 (8C, CH), 132.9 (4C, CH), 138.8 (2C, Cquat), 139.3 (2C, Cquat), 140.1 (2C, Cquat), 140.2 (2C, Cquat), 140.4 (2C, Cquat), 140.9 (2C, Cquat); MS (3-nitrobenzyl alcohol) m/z (%): 694 (¹³²Br₃M⁺, 21.3), 692 (¹³¹Br²Br²M⁺, 36), 690 (¹³⁷Br²M⁺, 17.6). HRMS Found: 692.0543. Calcd. for

DOI: 10.9790/5736-120412442 www.iosrjournals.org 29 Page
Dimethyl naphthalene-1,2 dicarboxylate (39a). A mixture of benzo[b]thiophene S,S-dioxide (34a, 194 mg, 1.17 mmol) and dimethyl acetylenedicarboxylate (23b, 1.2 g, 8.4(5) mmol) in diphenyl ether (1.5 g) was heated at 135 °C for 16h. Thereafter the cooled reaction mixture was subjected to column chromatography to give 39a (140 mg, 49%) as a colorless oil; 1H-NMR (270 MHz, CDCl3) δ 3.98 (3H, s, CO2CH3), 4.10 (3H, s, CO2CH3), 7.60 – 7.65 (2H, m), 7.89 – 7.93 (2H, m), 7.96 (1H, d, J = 8.6 Hz), 8.04 (1H, d, J = 8.6 Hz); 13C-NMR (67.8 MHz, CDCl3) δ 52.8 (OCH3), 52.9 (OCH3), 124.8 (Cquat), 125.0 (CH), 126.2 (CH), 127.8 (CH), 128.1 (CH), 128.6 (CH), 129.4 (Cquat), 129.6 (CH), 135.0 (Cquat), 135.2 (Cquat), 166.4 (Cquat), CO, 169.7 (Cquat, CO). MS (EI, 70 eV) m/z (%): 244 (M+), 21.

Dimethyl 4-phenyl naphthalene-1,2 dicarboxylate (39b). A solution of 3-phenylbenzo[b]thiophene S,S-dioxide (35d, 233 mg, 0.82 mmol) and dimethyl acetylenedicarboxylate (23b, 2.56 g, 17.7 mmol) in diphenyl ether (2.5 g) was heated at 140 °C for 15 h. The cooled mixture was submitted to chromatography on silica gel (hexane → hexane/CHCl3 1:1) to give 39b (70%) as a colorless oil; 1H-NMR (270 MHz, CDCl3) δ 3.96 (3H, s, CO2CH3), 4.11 (3H, s, CO2CH3), 7.46 – 7.62 (7H, m), 7.94 (2H, d, J = 8.4 Hz), 7.98 (1H, s); 13C-NMR (67.8 MHz, CDCl3) δ 52.7 (CO2CH3), 53.0 (CO2CH3), 125.9 (CH), 126.5 (2C, CH), 127.6 (CH), 128.0 (CH), 128.5 (2C, CH), 128.6 (CH), 131.6 (Cquat), 133.4 (Cquat), 136.7 (Cquat), 138.7 (Cquat), 139.0 (Cquat), 142.1 (Cquat), 166.3 (Cquat, CO), 169.7 (Cquat, CO).

Dimethyl 4-(acetylphenyl)naphthalene-1,2 dicarboxylate (39c). A solution of 3-(4-acetylphenyl)benzo[b]thiophene S,S-dioxide (35c, 225 mg, 0.79 mmol) and dimethyl acetylenedicarboxylate (23b, 800 mg, 5.54 mmol) in diphenyl ether (1.5 g) was heated at 135 °C for 26 h. The cooled solution was subjected directly to column chromatography on silica gel (hexane → CHCl3/ether/hexane 2:1:1) to give 39c as a colorless solid (157 mg, 55%), mp. 143 °C; 270 (3H, s, CO2CH3), 3.97 (3H, s, CO2CH3), 4.12 (3H, s, CO2CH3), 7.55 – 7.65 (2H, m), 7.59 (2H, d, J = 8.4 Hz), 7.86 (1H, d, J = 7.8 Hz), 7.95 (1H, d, J = 8.4 Hz), 7.99 (1H, s), 8.10 (2H, d, J = 8.4 Hz); 13C-NMR (67.8 MHz, CDCl3) δ 26.7(5) (CH3), 52.8 (OCH3), 53.0 (OCH3), 124.0 (Cquat), 125.8 (CH), 126.0 (CH), 126.6 (CH), 127.8 (CH), 128.5 (2C, CH), 128.9 (CH), 129.7 (Cquat), 130.2 (2C, CH), 133.1 (Cquat), 134.8(5) (Cquat), 136.4(5) (Cquat), 140.7 (Cquat), 144.2 (Cquat), 165.9 (CO2CH3), 169.4 (CO2CH3), 197.7 (Cquat, CO).

Di-n-propyl 4-phenyl naphthalene-1,2 dicarboxylate (39d). A mixture of 3-phenylbenzo[b]thiophene S-oxide (33, 160 mg, 0.70(5) mmol) and dipropyl acetylenedicarboxylate (23a, 1.19 g, 6.0 mmol) in diphenyl ether (0.75 g) was heated at 135 °C for 8h. Thereafter, the cooled solution was separated by column chromatography on silica gel (hexane → hexane/CHCl3 1:1) to give 39d (162 mg, 61%) as a slowly solidifying oil; 1H-NMR (270 MHz, CDCl3) δ 1.02 (6H, q, J = 6.2 Hz, 2 CH3), 1.76 – 1.87 (4H, m), 4.32 (2H, t, J = 7.0 Hz, OCH2), 4.49 (2H, t, J = 7.0 Hz, OCH2), 7.46 – 7.67 (7H, m), 7.93 (1H, d, J = 8.6 Hz), 7.98 (1H, s); 13C-NMR (67.8 MHz, CDCl3) δ 10.5 (CH3), 10.5 (CH3), 21.9 (CH3), 22.0 (CH3), 67.3 (OCH3), 67.6 (OCH3), 124.5 (Cquat), 125.8 (CH), 126.4 (CH), 127.4(5) (CH), 127.8(5) (CH), 128.3(5) (CH), 128.4(2C, CH), 128.9(5) (Cquat), 129.9 (2C, CH), 133.5 (Cquat), 134.4 (Cquat), 139.5 (Cquat), 141.8 (Cquat), 165.8 (Cquat, CO), 169.2 (Cquat, CO); MS (FAB, 3-nitrobenzyl alcohol) m/z (%): 377 (MH+ 15.9), 376 (M+, 45.3), 317 (32.3), 275 (100). HRMS: Found: 376.1671. Calcd. for C32H32O4: 376.1675 (FAB).

5-Phenylen-benz[a]anthracene-7,12-dione (40a). A solution of 3-phenylbenzo[b]thiophene S-oxide (33, 142 mg, 0.64 mmol) and naphthoquinone (41, 120 mg, 0.75 mmol) in diphenyl ether (900 mg) was heated at 135 °C for 9h. Thereafter, the cooled solution was subjected to column chromatography on silica gel (hexane → hexane/CHCl3 1:1) to give 40a (143 mg, 67%) as a colorless solid, mp. 167 °C [Lit. 167-167.5 °C [25,26] 1H-NMR (270 MHz, CDCl3) δ 7.54 (5H, bs), 7.57 – 7.63 (1H, m), 7.74 – 7.84 (3H, m), 8.00 (1H, d, J = 8.6 Hz), 8.27 (1H, d, J = 7.0 Hz), 8.33 (1H, d, J = 6.0 Hz), 8.35 (1H, s), 9.81 (1H, d, J = 8.9 Hz); 13C-NMR (67.8 MHz, CDCl3) δ 123.5 (CH), 126.4 (CH), 126.9 (CH), 127.3 (CH), 128.3 (CH), 128.5 (2C, CH), 128.7 (CH), 128.9 (CH), 129.5 (CH), 129.8 (2C, CH), 131.2(5) (Cquat), 132.2(5) (Cquat), 133.3 (Cquat), 133.4 (CH), 134.3 (CH), 135.0 (Cquat), 135.2 (2C, CH), 135.9(5) (2C, CH), 184.0 (Cquat, CO), 186.0 (Cquat, CO).

5-(4-Methoxyphenyl)-benz[a]anthracene-7,12-dione (40b). A solution of 3-(4-methoxyphenyl)benzo[b]thiophene S,S-dioxide (35a, 174 mg, 0.64 mmol) and naphthoquinone (41, 120 mg, 0.75 mmol) in diphenyl ether (900 mg) was heated at 135 °C for 42h. Thereafter, the cooled mixture was subjected to column chromatography on silica gel (hexane → hexane/CHCl3 1:1) to give 40b (151 mg, 65%) as a colorless solid [27] 1H-NMR (270 MHz, CDCl3) δ 3.93 (3H, s, OCH3), 7.09 (2H, d, J = 8.6 Hz), 7.48 (2H, d,
5-Bromobenzanthracene-7,12-dione (40c). — A solution of 3-bromobenzanthracene S,S-dioxide (34b, 245 mg, 1.0 mmol) and naphthaquinone (41, 198 mg, 1.25 mmol) in diphenyl ether (1.2 g) was heated at 135 °C for 34 h. Thereafter, the cooled mixture was subjected to column chromatography on silica gel (hexane → hexane/CHCl3 1:1) to give 40c (190 mg, 56%) as a solid, mp 198 °C (28.29). 1H-NMR (270 MHz, CDCl3) δ 7.77 – 7.84 (4H, m), 8.25 – 8.32 (2H, m), 8.39 – 8.43 (1H, m), 8.71 (1H, s), 9.75 (1H, d, 3J = 9.7 Hz); 13C-NMR (67.8 MHz, CDCl3) δ 126.6 (CH), 126.9 (CH), 127.4 (CH), 128.0 (CH), 128.7 (Cquin), 129.2 (CH), 130.0 (CH), 130.5 (CH), 131.4 (Cquin), 131.7 (Cquin), 131.8 (Cquin), 135.0 (C, Cquin), 133.7 (CH), 134.5 (CH), 182.4 (Cquin, CH), 185.6 (Cquin, CO); MS (EI, 70 eV) m/z (%) 358 ([35Br]M+, 97.1), 336 ([35Br]M+, 100), 257 (M-Br, 29.5), 202 (62.1). HRMS Found: 335.9788. Calcd. for C19H9O2Br: 335.9786.

1-(4-Ethoxyphenyl)-4-phenyl naphthalene (42). — A solution of 3-(4-ethoxyphenyl)benzanthracene S,S-dioxide (35b, 143 mg, 0.5 mmol) and phenylacetylen (38e, 500 mg, 5.0 mmol) in diphenyl ether (500 mg) was heated to 175 °C for 13h. The cooled mixture was subjected to column chromatography on silica gel (hexane → hexane/CHCl3 1:1) to give 42 (78%) as a colorless solid, mp 125 °C; 1H-NMR (600 MHz, CDCl3) δ 1.52 (3H, t, 3J = 6.9 Hz, CH3), 4.14 (2H, q, 3J = 6.9 Hz, OCH2), 7.04 (2H, d, 3J = 8.4 Hz), 7.42 – 7.54 (11H, m), 7.95 – 7.96 (1H, m), 7.99 – 8.00 (1H, m) 13C-NMR (150.9 MHz, CDCl3, DEPT) δ 14.9 (CH3), 63.5 (OCH2), 114.3 (2CH), 125.7 (CH), 125.7 (S), 126.3 (CH), 126.4 (CH), 126.5 (CH), 126.7 (CH), 127.2 (CH), 128.3 (2CH), 130.1 (2CH), 131.1 (2CH), 131.9 (5) (Cquin), 132.1 (Cquin), 133.0 (Cquin), 139.5 (Cquin), 140.9 (Cquin), 158.3 (Cquin). MS (EI, 70 eV) m/z (%) 324 (M+, 8.6), 83 (100). HRMS Found: 324.1517. Calcd. for C22H18O2: 324.1514.

2-(4-Iodophenyl)-5-phenyl-1H-benz[e]isooindole-1,3(2H)-dione (45). — A solution of 3-phenylbenzanthracene S-oxide (33, 120 mg, 0.54 mmol) and N-(4-iodophenyl)maleimide (43, 323 mg, 1.08 mmol) in diphenyl ether (1.0 g) was heated at 135 °C for 13h. The mixture was subjected to column chromatography on silica gel (hexane → hexane/CHCl3 1:1) to give 44 (120 mg, 47%) 1H-NMR (270 MHz, CDCl3) δ 7.31 (2H, d, 3J = 7.6 Hz), 7.52 – 7.55 (4H, m), 7.57 (1H, dd, 3J = 8.6 Hz, 3J = 7.3 Hz), 7.77 (1H, d, 3J = 8.4 Hz, 3J = 7.3 Hz), 7.86 (2H, d, 3J = 7.6 Hz), 7.91 (1H, s), 8.03 (1H, d, 3J = 8.6 Hz), 9.09 (1H, d, 3J = 8.4 Hz); 13C-NMR (67.8 MHz, CDCl3) δ 91.2 (Cquin), 120.5 (CH), 126.1 (CH), 128.2 (CH), 129.0 (2CH), 129.3 (CH), 129.5 (2CH), 129.6 (Cquin), 129.8 (CH), 130.3 (CH), 130.4 (Cquin), 130.6 (2CH), 131.3 (Cquin), 135.9 (Cquin), 139.1 (2CH, CH), 139.9 (Cquin), 149.3 (Cquin), 157.6 (Cquin), 165.9 (Cquin, CO), 168.4 (Cquin, CO); MS (EI, 70 eV) m/z (%) 475 (M+, 100), 431 (7.9), 430 (6.8), 334 (20.7), 304 (12.8), 276 (8.0), 202 (25). HRMS Found: 475.0816. Calcd. for C32H25ClO4Ni: 475.0609.

Benzyl 2,6-bis(tert-butyl)benzoate (47). — A solution of 2,5-bis(tert-butyl)thiophene S,S-dioxide (46, 250 mg, 1.11 mmol) and benzyl propiolate (26, 120 mg, 0.75 mmol) in diphenyl ether (500 mg) was heated at 170°C for 1h. The cooled solution was subjected to column chromatography on silica gel to give 47 (177 mg, 73%) as a colorless oil; 1H-NMR (270 MHz, CDCl3) δ 1.25 (9H, s, Bu′), 1.35 (9H, s, Bu′), 5.35 (2H, s), 7.27 (1H, m), 7.33 – 7.47 (6H, m), 7.34 (1H, s); 13C-NMR (67.8 MHz, CDCl3) δ 31.1 (3CH, Bu′), 31.4 (3CH3, Bu′), 34.2 (Cquin), 35.5 (Cquin), 125.5 (CH), 126.7 (CH), 126.9 (CH), 128.3 (CH), 128.5 (2CH, CH), 128.6 (2CH, CH), 132.2 (Cquin), 135.5 (Cquin), 144.5 (Cquin), 148.1 (Cquin), 172.1 (Cquin, CO), MS (EI, 70 eV) m/z (%) 324 (M+, 309 (M-CH3, 30), 217 (31), 91 (C6H5CH2CO2H, 100). HRMS Found: 324.2086. Calcd. for C22H22O2: 324.2089.

III. Results and Discussion

Preparation of starting materials

Tetraarylcyclopentadienones (tetracycrones) 7 were prepared according to a known strategy [14,30] via Weiss reaction with a concomitant double dehydration. The preparation of the tetracycrones used in this study, utilizing benzyltrimethylammonium hydroxide (BzlMe3NOH), has been published earlier [7] (Scheme 1).
The preparation of substituted diphenylacetylenes, where not commercially available to us, proceeded via double Sonogashira coupling reaction, using trimethylsilylacetylene as a mono-protected acetylene, where the TMS group was removed routinely (TBAF, THF, H2O) and the deprotection was followed by a second Sonogashira coupling reaction (Scheme 2). A similar strategy was followed in preparing 3-ethynyldibenzo\[b,d\]thiophene (20). In the case of mono-p-cyanotolane 15 and 3-ethynyldibenzo[b,d]thiophene (20), further derivatization occurred by hydrolysis of the cyano group in 15 to the amide 16 and by oxidation of the sulfur function in 20 to the S,S-dioxide 21, in order to have further tolane and arylacetylene derivatives available that could function as dienophiles in the subsequent [4+2]-cycloaddition reactions (Scheme 3). Lateron it was realized that it is more facile to derivatize these functions after the cycloaddition reactions, i.e. using alkynes 15 and 20, respectively, has been completed. Dipropyl acetylenedicarboxylate (23a) was best prepared by sulfuric acid catalyzed esterification of acetylenedicarboxylic acid (22), while DMAP catalyzed esterification of 22 in the presence of DCC gave very poor results. This in contrast to benzyl propiolate (26), which could be prepared from propiolic acid (24) in the presence of DMAP/DCC [31] (Scheme 4).

**Scheme 1.** Preparation of tetrarlycyclopentadienones (tetracyclones) 7 via Weiss reaction [7,14].

**Scheme 2.** Preparation of cyano and carboxamido-substituted diphenylacetylenes 15-17.

**Scheme 3.** Preparation of 3-ethynyldibenzo[b,d]thiophenes 20 and 21.

DOI: 10.9790/5736-1204012442
3-Substituted benzo[b]thiophenes 30 were synthesized by Suzuki-Miyaura reaction of either benzo[b]thienyl-3-boronic acid (31) and bromoarenes such as 32 or of 3-bromobenzo[b]thiophene (28), which can be synthesized directly from the commercially available benzo[b]thiophene (Br2, CHCl3 [32] or NBS, AcOH, CHCl3 [16]), with commercially available aryloboronic acids 29 (Scheme 5). The preparation of 3-phenylbenzo[b]thiophene S-oxide 33 from 3-phenylbenzo[b]thiophene 30a followed an established route. Mostly, benzo[b]thiophene S-oxides have been prepared from benzo[b]thiophenes by oxidation, where it is important to avoid over-oxidation to the respective benzo[b]thiophene S,S-dioxide. This can be achieved by using the oxidizing reagents H2O2 – AcOH [33], H2O2 – SeO2 [33], dimethylidioxirane (DMD, albeit in low yields), oxaziridines [33], BuOCl – MeOH [34,35], m-CPBA-BF3etherate [13,36], or by using enzymatic oxidation (P. putida UV4) [37,38]. In the present case, the benzo[b]thiophene 30a was oxidized to the benzo[b]thiophene S-oxide 33 with H2O2 – CF3CO2H [39] (Scheme 6), under conditions also used to oxidize thiophenes to thiophene S-oxides [40,41]. Benzo[b]thiophene S-oxide 33 could be obtained in acceptable yield (Scheme 6). The benzo[b]thiophene S-oxide is stable over an extended period of time. It should kept away from light, however, because as is the case of thiophene S-oxides [36], photoirradiation can lead to deoxygenation to revert the compounds back to the benzo[b]thiophene 30a. Benzo[b]thiophene S,S-dioxides 34/35 are formed by oxidation of benzo[b]thiophenes 27,28,30a-d with m-CPBA at room temperature (Scheme 7). In the same way, 2,5-tert-butylthiophene S,S-dioxide [42,43] was prepared.

Scheme 5. Preparation of 3-arylbenzo[b]thiophenes 30 by Suzuki-Miyaura reaction
Cycloaddition reactions of tetracyclones, benzo[b]thiophene S-oxides, and benzo[b]thiophene S,S-

Scheme 6. Preparation of 3-phenylbenzo[b]thiophene S-oxide (33) according to ref. 21.

![Scheme 6](image)

Scheme 7. Preparation of 3-substituted benzo[b]thiophene S,S-dioxides 34a,b and 35a-d.

Cycloaddition reactions

Tetraarylcyclopentadienones (tetracyclones) 7 are known to be excellent dienes in a Diels-Alder type reaction leading to cycloadducts with neighboring bulky substituents [44-46], with the reaction possessing a long history [47]. Nevertheless, the cycloaddition reactions often necessitate high temperatures. A typical solvent suitable for such high temperatures is diphenyl ether, which the author had used previously in cycloaddition reactions with bulky substituted cyclic dienes [43]. Diphenyl ether had also been used before in cycloaddition reactions with tetracyclones [46]. However, it has also been found that under the high temperatures used (>160 °C), tetracyclones convert to α-tetraarylpyrones, when the reactions are run in air [7].

The current experiments showed a very clear dependence of the reaction on the steric demand of the cycloaddends, namely on whether the alkyne used was mono- or disubstituted, where mono-substituted alkynes were very quick to react. This included the 1,4-diphenylbuta-1,3-diyne, where the reaction was complete after 3 hours. Nevertheless, in the cases studied, a reaction temperature of 175°C seemed optimal. In those cases, where microwave irradiation was used, the reaction time could be shortened, but the yields were generally not improved. Exclusion of air is necessary, especially when working with solvents such as diphenyl ether. In a number of cases, sublimation of the alkyne was found to be an issue. In those cases, it was advantageous to use diphenyl ether as solvent. In a number of cases, the mixture of cycloaddends did not form a homogeneous melt at 175 °C. Again, in these cases diphenyl ether was used as solvent. In cases, where functionalities were to be transformed by hydrolysis or oxidation, it was advantageous to undertake the cycloaddition reaction first and carry out the functional transformation second. This held true in both the cases where a carboxamiidohexaarylbenzene was used and where a S,S-dioxidibenzothienylpentaphenylbenzene was to be prepared. The amido-substituted tolanes such as 16 are less soluble than the respective cyano-substituted tolanes, and they also have higher melting points. Both of these characteristics are detrimental to the cycloaddition reaction. In the case of sulfone 21, the stability of the alkyne at elevated temperatures is a further impediment. Overall, the novel oligoarylbenzences 36 were prepared in good yield (Scheme 8).

Having worked with both tetracyclones and tetraarylthiophene S-oxides [43,48], the query always comes up – which is the better building block for hexaarylbenzenes and similar compounds? Competitive experiments in the cycloaddition of tetraphenylcycloptenta-1,3-diene and tetraphenyliothiophene S-oxide with N-phenylmaleimide have shown that tetraphenylthiophene S-oxide is the more reactive diene [43]. Nevertheless, where extended reaction times are needed, thiophene S-oxides tend to give more side-products, which include the respective thiophenes as deoxygenation products. The preparation procedures of tetraarylthiophene S-oxide and tetracyclone complement each other – while both can be prepared by the reaction of zirconapentadienes, the more robust route is the Weiss reaction for tetracyclones, which is complemented by the oxidation reaction of
Cycloaddition reactions of tetracyclones, benzo[b]thiophene S-oxides, and benzo[b]thiophene S,S-

Yields can be comparable. Tetracyclones can be stored over longer periods of time than tetraarylthiophene S-oxides which deoxygenate slowly even at room temperature, especially when exposed to (day)light [36,49].

![Chemical structure](image)

[36a] 7a
[36b] 36b: R = CN (89%)
[36c] 36c: R = CN (85%)
[36d] 36d: R = CN (85%)
[36e] 36e: R = CONH$_2$ (73%)
[36f] 36f: R = CONH$_2$ (71%)
[37a] 37a: R = CONH$_2$ (87%)
[37b] 37b: R = CONH$_2$ (73%)
[37c] 37c: R = CONH$_2$ (71%)
[37d] 37d: R = CONH$_2$ (71%)

DOI: 10.9790/5736-1204012442 www.iosrjournals.org 35 | Page
Cycloaddition reactions of tetracyclones, benzo[b]thiophene S-oxides, and benzo[b]thiophene S,S-

\[ \text{7a} \rightarrow \text{38a} \text{ (88\%)} \]

\[ \text{H}_2\text{CO} - \text{7a} \rightarrow \text{H}_2\text{CO} - \text{36e} \]

\[ \text{7a} \rightarrow \text{38b} \text{ (91\%)} \]

\[ \text{H}_2\text{C} - \text{7a} \rightarrow \text{H}_2\text{C} - \text{36f} \]

\[ \text{7a} \rightarrow \text{36g \ (X = 0 \ (64\%))} \]

\[ \text{7a} \rightarrow \text{36h \ (X = 2 \ (91\%))} \]

\[ \text{20} \rightarrow \text{175 \ C, 10h \ (81\%)} \]

\[ \text{F} - \text{7c} \rightarrow \text{F} - \text{36h \ (81\%)} \]

DOI: 10.9790/5736-1204012442 www.iosrjournals.org 36 | Page
Cycloaddition reactions of tetracyclones, benzo[b]thiophene S-oxides, and benzo[b]thiophene S,S-

[Chemical structures and reactions depicted in the image]
Furthermore, 3-substituted benzo[b]thiophene S,S-dioxides 34a, and 35b-d as well as benzo[b]thiophene S-oxide 33 were tested as dienes in cycloaddition reactions with alkynes. A number of 2-substituted benzo[b]thiophenes had been tested as dienes, previously [13]. Again, the benzo[b]thiophene S-oxide 33 was seen to be more reactive than the corresponding benzo[b]thiophene S,S-dioxides, eg. 34a, 35c , and 35d, which is reflected in the reaction times (Scheme 9). The reaction of benzo[b]thiophene S-oxide 33 and benzo[b]thiophene S,S-dioxides 35a and 35b with p-naphthoquinone (41) gave 5-substituted benz[a]anthracene-7,12-diones 40. The long reaction times in diphenyl ether in the presence of air leads to the oxidation of the primary cycloadducts to produce compounds 40 (Scheme 10). This does not happen in the cycloaddition with other alkenes such as exemplified by the cycloaddition of benzo[b]thiophene S-oxide 33 with N-(p-iodophenyl)maleimide (43), where the cycloadduct 44 is stable under the reaction conditions and an oxidant (in this case, DDQ) is needed for a subsequent dehydrogenation (Scheme 12). Interestingly, the cycloaddition of benzo[b]thiophene S,S-dioxide 35b to phenylacetylene (38e) only gave one isolable product, showing a very regioselective reaction (Scheme 11). The structure of the compound was confirmed by an HMBC-NOESY sequence, where an NOE effect was detected between the ortho protons of the aryl substituents with the inner protons of the naphthalenyl-unit as shown in Figure 2. It is believed that the regioselectivity of this reaction stems from a secondary overlap of frontier orbitals of the phenyl group of the phenyl acetylene and the benzo unit of.

Scheme 8. Cycloaddition of tetracyclones 7 to diarylacetylenes and arylacetylenes.
Cycloaddition reactions of tetracyclones, benzo[b]thiophene S-oxides, and benzo[b]thiophene S,S- 

dioxide as shown in Figure 2. A similar regioselectivity had been noted in the cycloaddition of phenylacetylene with phenyl-substituted 2-pyrones [50].

Finally, the reactivity of 2.5-tert-butylthiophene S,S-dioxide (47) as a cyclic diene with two sterically exacting alkyl substituents towards propiolate 26 was investigated (Scheme 13) and compared to the reactivity of the corresponding thiophene S-oxide [43]. It was seen that 47 reacts facilely with mono-substituted alkynes such as 26 at elevated temperatures.

Cycloaddition reactions of tetracyclones, benzo[b]thiophene S-oxides, and benzo[b]thiophene S,S-

Scheme 10. Benzo[b]thiophene S,S-dioxides and benzo[b]thiophene S-oxide as dienes in Diels Alder type reactions with acetylene dicarboxylates

Scheme 11. Regioselective Diels-Alder reaction of benzo[b]thiophene S,S-dioxide 35b with phenylacetylene

Figure 2. Regioselective formation of 1-(4-ethoxyphenyl)-4-phenylnaphthalene (42)

Scheme 12. Cycloaddition of benzo[b]thiophene S-oxide 33 and phenylmaleimide 43 with subsequent oxidative dehydrogenation of the cycloadduct
Cycloaddition reactions of tetracyclones, benzo[b]thiophene S-oxides, and benzo[b]thiophene S,S-

Scheme 13. Cycloaddition of 2,5-bis(tert-butyl)thiophene S,S-dioxide (47) to alkyne 26

IV. Conclusion

A number of tetracyclonopentadienones (tetracyclones) 7 were reacted with alkynes to generate oligoarylbenezes 36/37, among them the novel compounds 36b/37b, 36g/37d, 36h, 36j, 36k, 36l, 36m, 36n, and 36o. The reactions were carried out under inert atmosphere. These reactions were performed under solventless conditions unless the reaction mixtures did not give homogeneous melt or the alkyne was easily sublimated. In those cases, de-aerated diphenyl ether was used as a solvent. A 3-arylbenzo[b]thiophene S-oxide and a number of 3-arylbenzo[b]thiophene S,S-dioxides were prepared by a Suzuki cross-coupling reaction / oxidation sequence. These compounds were used as dienes in their reaction with alkynes, leading to substituted naphthalenes. Their reactions with p-naphthoquinone at elevated temperatures using diphenyl ether as solvent lead to benz[a]anthracene-7,12-diones. With phenylacetylene, 3-arylbenzo[b]thiophene S,S-dioxide 35b leads to a regioselective cycloaddition, most likely governed by secondary interactions between the phenyl group of the alkyne and the benzo unit of the benzo[b]thiophene S,S-dioxide.

Acknowledgement

The author thanks Ms. Kyoko Ideta, Institute of Materials Chemistry and Engineering (IMCE), Kyushu University, for the carrying out of 2D-NMR experiments (NOESY and HMOC) on compound 42.

References


DOI: 10.9790/5736-1204012442 www-iosrjournals.org 41 [Page]
Cycloaddition reactions of tetracyclones, benzo[\textit{b}]thiophene \textit{S}-oxides, and benzo[\textit{b}]thiophene \textit{S}-


[40]. W. J. M. van Tolborg, Improved method for the synthesis of dialkyl-substituted thiophene 1,1-dioxides, Synthetic Communications, 1977, 6, 583 – 589.


