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A Palladium(0)–Samarium(II) System for the Preparation of Allenes from Propargylic Acetates: Application to the Synthesis of 2,3-Naphthoquinodimethanes

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The selective conversion of 1,2-bis(1′-acetoxy-2′-propynyl)benzene derivatives to the corresponding 1,2-diallenylbenzenes with the aid of a palladium(0)–samarium(II) reduction system leads to a new route to fairly reactive *o*-naphthoquinodimethane derivatives under mild conditions. The reactions of these naphthoquinodimethanes were found to follow different paths depending on the nature of the substituents on the terminal acetylenic carbon atoms. They undergo intermolecular Diels–Alder reactions with various dienophiles, intramolecular [2+2] cycloadditions, or intramolecular [1,5]-sigmatropic hydrogen shifts.

Keywords: 2,3-naphthoquinodimethane; Pd(0)–SmI_2 system; allene synthesis; cycloaddition; 1,2-diphenylnaphtho[*b*]cyclobutene; [1,5]-hydrogen shift

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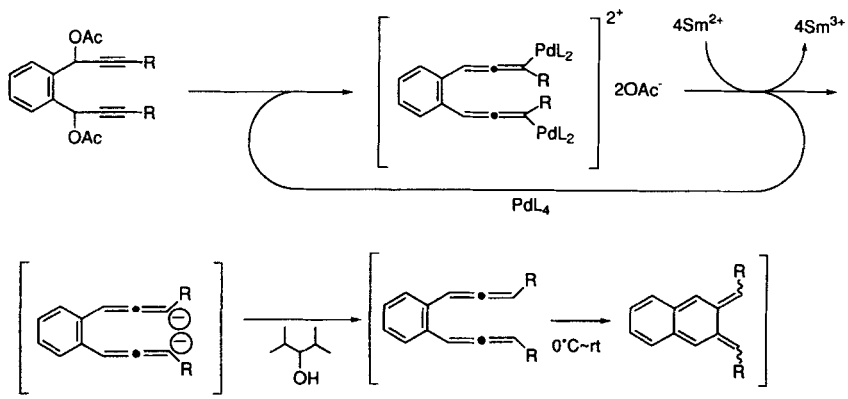
INTRODUCTION

Recently we reported that propargylic acetates could be reduced by samarium(II) iodide (SmI_2) in the presence of a variety of electrophiles and a catalytic amount of palladium(0) [Pd(0)] to give the corresponding allene and acetylene derivatives.[1] This finding prompted us to examine a new route to *o*-quinodimethanes, i.e. a SmI_2-promoted selective formation of 1,2-diallenylbenzenes from the corresponding propargylic acetates followed by their 6π-electron cyclization.[2] *o*-Quinodimethanes have been known to serve as effective dienes in the Diels–Alder reaction because of their extreme reactivities due to the restoration of aromacity on the cycloaddition.[3] Therefore they have been widely used, for example, for the construction of steroidal frameworks.[4–8] However, only a limited number of methods have been reported for the generation of these reactive species. In this paper a mild and convenient one-pot method for the



Scheme 1 Strategy.

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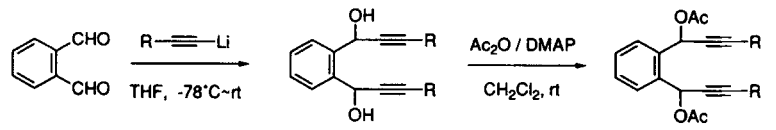


1a	R = H	91 %	**2a**	R = H	87 %
1b	R = Ph	96 %	**2b**	R = Ph	81 %
1c	R = C_6H_{13}	74 %	**2c**	R = C_6H_{13}	94 %

Scheme 2 Preparation of precursors. THF, tetrahydrofuran; rt, room temperature; DMAP, 4-dimethylaminopyridine.

generation of 2,3-naphthoquinodimethanes is described, and also their reactivities.[9]

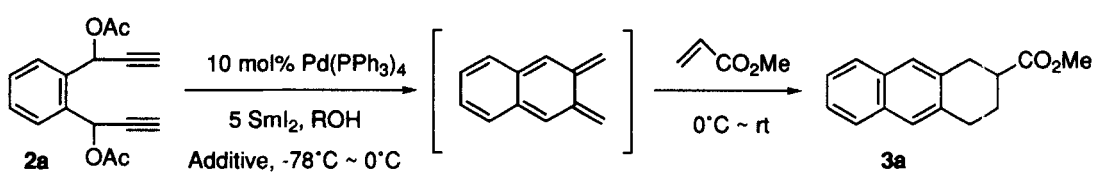
RESULTS AND DISCUSSION

The present approach consists of two reactions—the formation of *ortho*-diallenyl compounds and their electrocyclic reactions—as shown in Scheme 1. As the starting substrates, we adopted 1,2-bis(1′-acetoxy-2′-propynyl)benzene derivatives with differently substituted acetylene moieties (**2a–2c**). These substrates (R = H, Ph, n-C_6H_{13}) were prepared in two steps, as shown in Scheme 2. Introduction of acetylenic units to *o*-phthalaldehyde afforded the corresponding bispropargylic alcohols (**1a–1c**) in good yields. The hydroxyl groups were acetylated with acetic anhydride in the usual manner to give **2a–2c**.

With the starting substrates in hand, we first examined the reaction of 1,2-bis(1′-acetoxy-2′-propynyl)benzene (**2a**). Under an argon atmosphere, a SmI_2–THF solution was added to a solution of **2a**, a catalytic amount of $Pd(PPh_3)_4$ and 2,4-dimethyl-3-pentanol at −78 °C. When the resulting mixture was gradually warmed to 0 °C while being stirred, the starting material was completely consumed. An excess amount of methyl acrylate was added to this solution, and the resulting mixture was stirred at the same temperature and then at room temperature for several hours. A normal work-up (see the Experimental section), followed by preparative TLC purification gave the corresponding tricyclic Diels–Alder adduct (**3a**) in 63% yield. In addition, we obtained a mixture of by-products whose mass spectrum showed the existence of a dimeric product. However, we found it difficult to separate them in our hands. In order to improve the yield, a variety of proton sources and additives were examined (Table 1). When 2,6-di-*t*-butyl-4-methylphenol (BHT) and hexamethyl phosphoramide (HMPA) were employed as a proton source and an additive, respectively, the cycloadduct was obtained in a yield as high as 65% (Table 1, entry 4); however, the reproducibility was poor. Therefore we adopted the reaction conditions described in Table 1, entry 1, and carried out the cycloaddition with various dienophiles.

As shown in Table 2, the reaction is quite general and satisfactory yields were obtained except for the case of Table 2, entry 4. While the

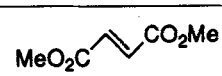
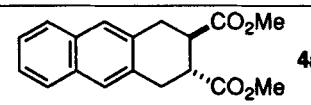
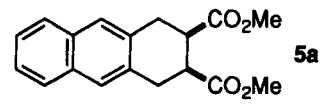
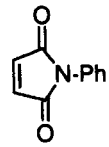
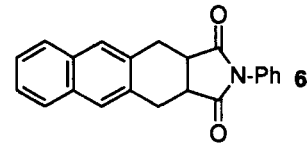
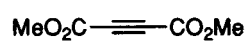
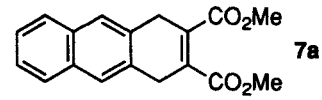
Table 1 Examination of proton sources and additives in Diels–Alder cycloaddition



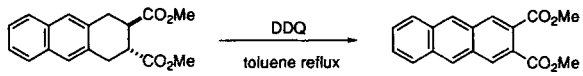
Entry	ROH	Additive	Yield (%)
1	2,4-Dimethyl-3-pentanol	None	63
2	2,4-Dimethyl-3-pentanol	HMPA	58
3	Ethylene glycol	None	25
4	BHT[a]	HMPA	65

[a] BHT, 2,6-di-*t*-butyl-4-methylphenol. [b] HMPA, hexamethylphosphoramide.

Table 2 One-pot conversion of **2a** to the cycloadducts (**4a–7a**)

Entry	Dienophile	Major product	Yield (%)
1		 **4a**	60
2		 **5a**	48[a]
3		 **6a**	59
4		 **7a**	17

[a] A mixture of diastereomers: *cis*:*trans* = 72:28.



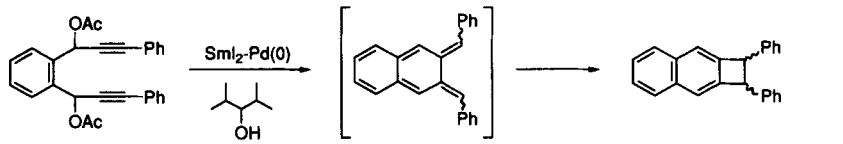
4a **8a** 77 %

Scheme 3 Aromatization of **4a**. DDQ, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

reaction with dimethyl fumarate afforded the 2,3-*trans* adduct (**4a**) as a single isomer (Table 2, entry 1), the use of dimethyl maleate produced a mixture of diastereomers (Table 2, entry 2). The reason for this is not clear at present; however, the contribution of the radical nature of naphthoquinodimethane may be excluded because of its high energy.[3] So, the isomerization may have occurred on the starting dienophile or the products, before or after the cycloaddition, respectively.

The *trans* adduct (**4a**) was easily converted to 2,3-dicarbomethoxyanthracene (**8a**) in good yield (Scheme 3).

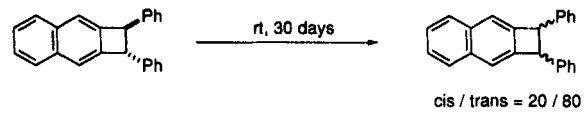
Next, the reactions of **2b** and **2c** were examined under the conditions described above. The reduction of **2b** proceeded smoothly; however, the corresponding [4+2] cycloadduct (**3b**) with methyl acrylate was not obtained at all. Instead, a mixture of *trans*- and *cis*-diphenylnaphtho-[*b*]cyclobutene was produced in 92:8 ratio as the result of intramolecular [2+2] cycloaddition of the *o*-naphthoquinodimethane intermediate. When the reduction was performed at room temperature and then the mixture was stirred at 65 °C for several hours without methyl acrylate, a mixture of the diastereomers (*trans*:*cis* = 84:16) was obtained in 66% yield (Scheme 4). The pure *trans*-isomer, upon standing for 30 days at room temperature, changed to an equilibrium mixture of diastereomers (Scheme 5), which indicates that cleavage and regeneration of the



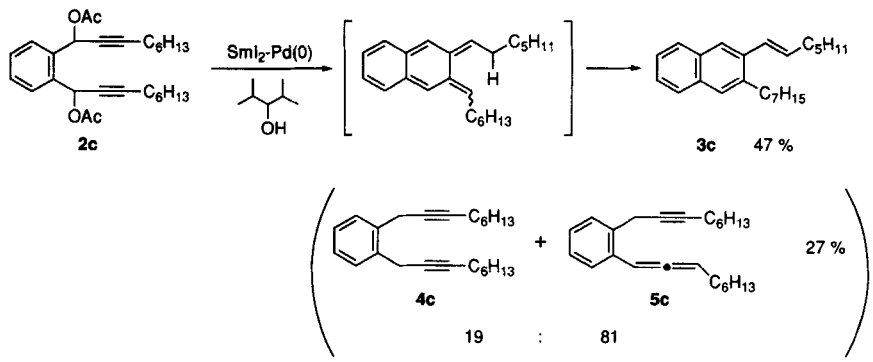
2b **3b**

-30°C ~ rt 59 % cis / trans = 8 / 92
rt 53 % cis / trans = 11 / 89
rt ~ 65°C 66 % cis / trans = 16 / 84

Scheme 4 Reaction of **2b**.



Scheme 5 Isomerization of *trans*-1,2-diphenylnaphtho[*b*]cyclobutene.



Scheme 6 Reaction of **2c**.

cyclobutene ring takes place thermally and/or photochemically, probably through a radical process.[10]

It has been verified by Cava *et al.* that heating of *trans*-diphenylnaphtho[*b*]cyclobutene at the boiling point of DMF generates the corresponding naphthoquinodimethane.[11]

The reaction of bispropargylic acetates with alkyl substituents (**2c**) also did not give the Diels–Alder adduct with methyl acrylate. The major product was the 1-alkenyl-2-alkylnaphthalene (**3c**) which stemmed from the corresponding naphthoquinodimethane intermediate via [1,5]-sigmatropic hydrogen shift.[12] A mixture of diacetylene and acetylene-allene derivatives, as minor products, was also isolated (Scheme 6).

EXPERIMENTAL

Melting points are uncorrected. ^{1}H NMR spectra were measured in a $CDCl_3$ solution on a JEOL JMN-EX270 or JMN-GX400. Chemical shifts are given by δ relative to internal Me_4Si. Mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained on a Shimadzu GCMS-QP1000EX and Shimadzu/Kratos Concept 1S, respectively. Solvents were purified before use and all reactions were conducted under argon.

1,2-Bis(1′-acetoxy-2′-propynyl)benzene (2a)

To a solution of **1a** (1.47 g, 7.88 mmol) and 4-dimethylaminopyridine (DMAP) (2.89 g, 28.63 mmol) in dichloromethane (50 ml) was added acetic anhydride (1.93 ml, 20.48 mmol) and the mixture was stirred at room temperature until completion of the reaction by monitoring with TLC on silica gel. After evaporation of the solvent, the remaining residue was treated with water and the crude product was extracted with ether. The extract was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (n-hexane:EtOAc = 5:1). The eluate was concentrated to give a slightly yellow solid, which was recrystallized from ether and n-hexane to give 1.68 g (6.22 mmol, 79%) of **2a** as a mixture of diastereomers.

^{1}H NMR: δ 7.63–7.75 (m, 2H), 7.40–7.47 (m, 2H), 6.75 (d, 1.1H, J = 2.31 Hz, benzylic), 6.73 (d, 0.9H, J = 2.31 Hz, benzylic), 2.69 (d, 0.9H, J = 1.98 Hz, ethynyl), 2.63 (d, 1.1H, J = 2.31 Hz, ethynyl), 2.31 (s, 3.3H, acetyl), 2.09 (s, 2.7H, acetyl).

1,2-Bis(1′-acetoxy-3′-phenyl-2′-propynyl)benzene (2b)

The reaction was carried out in a similar manner

to that described in the preparation of **2a**, to give **2b** (81%) as a yellow sticky oil.

^{1}H NMR: δ 7.70–7.79 (m, 2H), 7.40–7.47 (m, 6H), 7.21–7.33 (m, 6H), 7.06 (s, 2H, benzylic), 2.11 (s, 1.9H, acetyl), 2.09 (s, 4.1H, acetyl).

1,2-Bis(1'acetoxy-2'-nonynyl)benzene (2c)

The reaction was carried out in a similar manner to that described in the preparation of **2a**, to give **2c** (94%) as a yellow oil.

^{1}H NMR (400 MHz): δ 7.68–7.70 (m, 0.2H), 7.62–7.66 (m, 1.8H), 7.35–7.40 (m, 2H), 6.72–6.74 (m, 2H, benzylic), 2.24 (dt, 0.4H, J = 1.99, 7.17 Hz, propargylic), 2.20 (dt, 3.6H, J = 2.03, 7.25 Hz, propargylic), 2.10 (s, 5.4H, acetyl), 2.06 (s, 0.6H, acetyl), 1.45–1.54 (m, 4H, methylene), 1.21–1.37 (m, 12H, trimethylene), 0.87 (t, 0.6H, J = 6.87 Hz, methyl), 0.87 (t, 5.4H, J = 7.02 Hz, methyl).

2-Methoxycarbonyl-1,2,3,4-tetrahydroanthracene (3a)

A SmI_2–THF solution (0.1 mol l^{-1}, 9.25 ml, 0.925 mmol) was added slowly to a solution of **2a** (49.5 mg, 0.183 mmol), tetrakis(triphenylphosphine)palladium (22.0 mg, 0.019 mmol), and 2,4-dimethyl-3-pentanol (58.0 µl, 0.407 mmol) in THF (4 ml) at −78 °C. The mixture was stirred for 30 min at the same temperature and then gradually warmed to 0 °C, the consumption of the substrate being monitored by TLC. After completion of the reduction, a solution of methyl acrylate (50.0 µl, 0.555 mmol) in THF (2 ml) was added dropwise. The whole mixture was stirred at 0 °C for 2 h and then at room temperature for 12 h. To the reaction mixture was added n-hexane (2 ml) and SiO_2 (*ca* 1 g). The resulting suspension was stirred for 10 min and then passed through a pad of silica gel. The filtrate was concentrated and purified by preparative TLC on silica gel (n-hexane : EtOAc = 5 : 1) to give 27.9 mg (0.116 mmol, 63%) of **3a** as a slightly yellow solid, mp 113–117 °C.

^{1}H NMR: δ 7.68–7.75 (m, 2H), 7.58 (s, 1H), 7.56 (s, 1H), 7.34–7.40 (m, 2H), 3.74 (s, 3H, methoxy), 2.93–3.29 (m, 4H), 2.77–2.88 (m, 1H), 2.20–2.32 (m, 1H), 1.89–2.03 (m, 1H); MS, *m/z* 240 (M^+), 181, 180, 179, 178, 166, 165, 152, 89.

Analysis: calcd for $C_{16}H_{16}O_2$: C, 79.98; H, 6.71. Found: C, 79.86; H, 6.80%.

trans-2,3-Bis(methoxycarbonyl)-1,2,3,4-tetrahydroanthracene (4a)

The reaction was carried out in a similar manner to that described in the preparation of **3a**, to give **4a** (57%) as a slightly yellow solid, mp 122–124 °C (lit.[2a] mp 123–124 °C).

^{1}H NMR: δ 7.71–7.76 (m, 2H), 7.59 (s, 2H), 7.37–7.43 (m, 2H), 3.75 (s, 6H, methoxy), 3.11–3.37 (m, 6H). HRMS: *m/z* calcd for $C_{18}H_{18}O_4$, 298.1205 (M^+); found, 298.1211.

cis- and *trans*-2,3-Bis(methoxycarbonyl)-1,2,3,4-tetrahydroanthracenes (5a)

The reaction was carried out in a similar manner to that described in the preparation of **3a**, to give **5a** (48%, *cis* : *trans* = 72 : 28) as a white solid.

^{1}H NMR: δ 7.69–7.75 (m, 2H), 7.61 (s, 1.4H, *cis*), 7.59 (s, 0.6H, *trans*), 7.35–7.43 (m, 2H), 3.75 (s, 1.7H, methoxy, *trans*), 3.70 (s, 4.3H, methoxy, *cis*), 3.11–3.53 (m, 6H). MS: *m/z* 298 (M^+), 238, 180, 179, 178.

Analysis: calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.36; H, 6.05%.

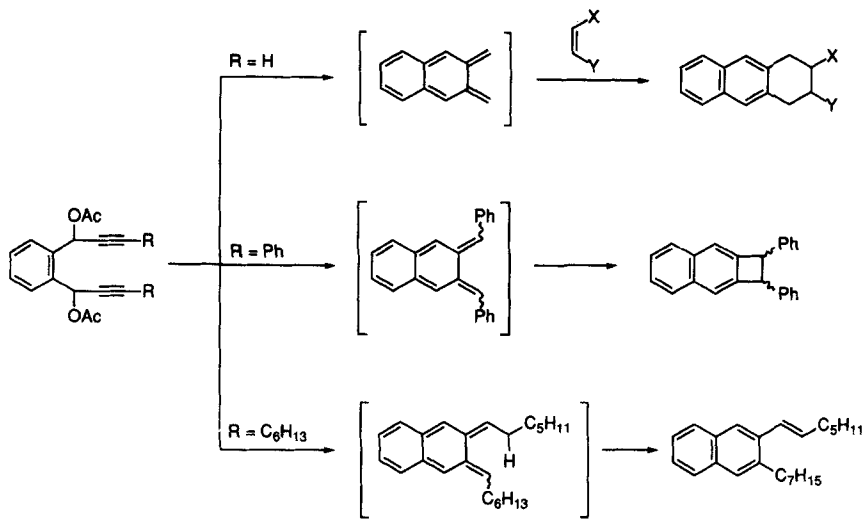
1,2,3,4-Tetrahydro-*N*-phenyl-2,3-anthracenedicarboximide (6a)

The reaction was carried out in a similar manner to that described in the preparation of **3a**, to give **6a** (59%) as a white solid, mp 242–244 °C.

^{1}H NMR: δ 7.76–7.79 (m, 2H), 7.67 (s, 2H), 7.43–7.46 (m, 2H), 7.23–7.29 (m, 3H), 6.74–6.79 (m, 2H), 3.55 (t, 2H, J = 2.64 Hz), 3.46 (s, 0.8H), 3.41 (s, 1.2H), 3.20–3.22 (m, 1.2H), 3.15–3.17 (m, 0.8H). MS: *m/z* 327 (M^+), 180, 179, 165, 152, 89. HRMS: *m/z* calcd for $C_{22}H_{17}NO_2$, 327.1259 (M^+); found 327.1269.

2,3-Bis(methoxycarbonyl)-1,4-dihydroanthracene (7a)

The reaction was carried out in a similar manner to that described in the preparation of **3a**, to give



Scheme 7 Summary.

7a (17%) as a yellow solid, mp 110–112 °C (lit.[13] mp 120–121 °C).

^{1}H NMR: δ 7.73–7.79 (m, 2H), 7.67 (s, 2H), 7.39–7.45 (m, 2H), 3.90 (s, 4H), 3.85 (s, 6H, methoxy). MS: *m/z* 296 (M^+), 265, 264, 263, 237, 236, 206, 205, 179, 178, 177, 176, 165, 151, 89, 88, 76, 59. HRMS: *m/z* calcd for $C_{18}H_{16}O_4$, 296.1052 (M^+); found, 296.1047.

2,3-Bis(methoxycarbonyl)anthracene (8a)

A mixture of **4a** (7.4 mg, 0.0248 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 12.0 mg, 0.0546 mmol) in toluene (2 ml) was refluxed for 5 h. The reaction mixture was cooled and concentrated. The residue was subjected to preparative TLC on silica gel (n-hexane: EtOAc = 2:1) to give 5.6 mg (0.0190 mmol, 77%) of **8a** as an orange solid, mp 151–153 °C (lit.[13] mp 151–152 °C).

^{1}H NMR: δ 8.51 (s, 2H), 8.44 (s, 2H), 8.02–8.08 (m, 2H), 7.54–7.59 (m, 2H), 3.98 (s, 6H, methoxy). HRMS: *m/z* calcd for $C_{18}H_{14}O_4$, 294.0892 (M^+); found, 294.0908.

cis- and *trans*-1,2-Diphenylnaphtho[*b*]-cyclobutenes (3b)

The reaction was carried out in a similar manner to that described in the preparation of **3a**, to give **3b** as a mixture of diastereomeres (59%, *cis*: *trans* = 8:92). Preparative TLC on silica gel (n-hexane: EtOAc = 5:1) provided cleanly the *trans*-cyclobutene; however, isolation of the *cis*-cyclobutene was unsuccessful.

^{1}H NMR of *trans*-isomer: δ 7.85–7.90 (m, 2H), 7.69 (s, 2H), 7.43–7.50 (m, 2H), 7.24–7.39 (m, 10H, phenyl), 4.68 (s, 2H). MS: *m/z* 306 (M^+), 305, 304, 303, 302, 290, 289, 230, 229, 228, 226, 149, 114, 57. HRMS: *m/z* calcd for $C_{24}H_{18}$, 306.1409 (M^+); found, 306.1428. Mp 157–159 °C (lit.[11] mp 158–159 °C).

The reaction of 2c

The reaction of **2c** was carried out in a similar manner to that described in the preparation of **3a** to give a mixture of **3c** (47%), **4c** (5%) and **5c** (22%). Preparative TLC on silica gel (n-hexane: EtOAc = 40:1) provided cleanly **3c**; however, separation of **4c** and **5c** was not attempted.

^{1}H NMR of **3c**: δ 7.84 (s, 1H), 7.70–7.78 (m, 2H), 7.55 (s, 1H), 7.34–7.40 (m, 2H), 6.70 (d, 1H, J = 15.51 Hz, benzylic–olefinic), 6.21 (dt, 1H, J = 6.93, 15.51 Hz, olefinic), 2.79 (t, 2H, J = 7.75 Hz, benzylic), 2.28 (dt, 2H, J = 6.93, 14.19 Hz, allylic), 1.29–1.75 (m, 16H, methylene), 0.86–0.95 (m, 6H, methyl).
^{1}H NMR of **4c** and **5c**: δ 7.13–7.47 (m, 8H), 6.36 (dt, 1.6H, J = 3.14, 6.38 Hz, benzylic-allenic), 5.53 (dt, 1.6H, J = 6.82, 13.53 Hz, allenic), 3.60 (t, 4.8H, J = 2.31 Hz, benzylic–propargylic),

2.08–2.24 (m, 8H, methylene), 1.22–1.77 (m, 32H, methylene), 0.86–0.91 (m, 12H, methyl).

CONCLUSION

A mild and convenient method for the generation of *o*-naphthoquinodimethanes has been developed on the basis of a Pd(0)–SmI_2-promoted allene synthesis. Scheme 7 shows that the destiny of the intermediates depends upon the substituent (R). These were trapped intermolecularly with a variety of dienophiles to give the corresponding Diels–Alder adducts (when R = H), intramolecular [2 + 2] cycloaddition affording the naphtho[*b*]cyclobutene derivative (when R = Ph), or bringing about a [1,5]-sigmatropic hydrogen shift to give the naphthalene derivative (when R = n-C_6H_{13}), respectively.

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