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On the Twofold Heck Reaction of 4-Vinylcyclohexene and *p*-Dihalobenzenes

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Dedicated to Prof. K.-H. Thiele on the Occasion of his 65th Birthday

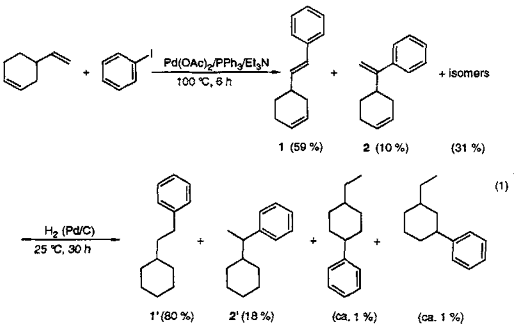
Abstract The palladium-catalyzed reaction of iodobenzene, *p*-haloiodobenzenes (*p*-C_6H_4IX'; X'=F, Cl, Br, I) and *p*-dibromobenzene with 4-vinylcyclohexene (Heck arylation reaction of olefins) was investigated with $Pd(OAc)_2/PR_3/Et_3N$ (R=phenyl, *o*-tolyl) as a classical catalyst system and with $Pd(OAc)_2$/KOAc/[$BzEt_3N$]Cl in DMF as a phase-transfer catalyst system, respectively. Iodobenzene reacts with 4-vinylcyclohexene to give (*E*)-2-(cyclohex-3-enyl)vinylbenzene (**1**) as main product. *p*-Haloiodobenzenes react with 4-vinylcyclohexene to give (*E*)-*p*-halo-2-(cyclohex-3-enyl)vinylbenzene (**3**), *p*-halo-1-(cyclohex-3-enyl)vinylbenzene (**4**) or (*E,E*)-*p*-bis[2-(cyclohex-3-enyl)vinyl]benzene (**5**) depending on the reaction conditions and the catalyst system used. The phase-transfer catalyst system is less reactive but more selective. A reaction temperature of 80 °C is necessary for reaction with *p*-dibromobenzene. The investigations demonstrate the much higher reactivity of the exocyclic double bond of 4-vinylcyclohexene in comparison with the endocyclic one.

Palladium-catalyzed C-C bond coupling reactions between olefins and halobenzenes are well-known as Heck reactions which proved to be a valuable approach for preparing substituted aryl olefins [1-3]. Especially $Pd(OAc)_2/PR_3$ (R=phenyl, *o*-tolyl) as catalyst system in the presence of an amine at temperatures between 100 and 150 °C was thoroughly investigated in the coupling reactions between olefins with terminal double bonds and iodo- or bromobenzenes. Larock introduced $Pd(OAc)_2$/alkali acetate/ammonium salt as phase-transfer catalytical systems for the Heck reaction of cycloalkenes which already work at room temperature [4-6].

We were interested in the twofold Heck reaction by using *p*-dihalobenzenes and 4-vinylcyclohexene as substrates to investigate the different reactivity of its endo- and exocyclic double bond. Apart from an acetoxylation reaction [7], homogenously palladium-catalyzed functionalization reactions of 4-vinylcyclohexene were not described.

Results and Discussion

4-Vinylcyclohexene reacts with iodobenzene under the influence of the "classical" Heck catalytical system ($Pd(OAc)_2/PPh_3/Et_3N$, 100 °C, 6 h) almost exclusively at the exocyclic double bond, cf. eq. 1. The main product of the reaction is (*E*)-2-(cyclohex-3-enyl)vinylbenzene (**1**). 1-(Cyclohex-3-enyl)vinylbenzene (**2**) is formed as a side product. Furthermore, an isomerization takes place to give double bond isomers of **1** and **2**. An attack of the endocyclic double bond to give 1-vinyl-4-phenylcyclohexenes and 1-vinyl-3-phenylcyclohexenes takes place only on a small extent (ca. 2 %), as was shown after hydrogenation of the reaction mixture on palladium-on-charcoal (eq. 1). When the reaction is performed at 150 °C (reaction time 3 d), an isomerization takes place to give the thermodynamically more stable product with conjugated double bonds (*E*)-2-(cylohex-1-enyl)vinylbenzene (41 % yield GC). This is a Pd-catalyzed reaction as was shown by separate experiments [8].

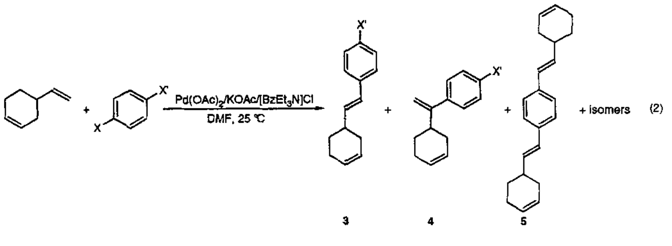


Compound **1** was isolated in a pure state by fractional crystallization at low temperatures from *n*-pentane. Its constitution was established by ^{1}H- and ^{13}C-NMR spectroscopy as well as by mass spectroscopy. The NMR data are in agreement with the data given in lit. [9] in which an (*E*)-(*Z*)-mixture of **1** was obtained via a Wittig reaction. The constitution of **2** was proved by comparison with an authentic sample prepared in a Wittig reaction starting from 4-cyclohexenylphenyl ketone.

The phase-transfer catalytical system of Larock ($Pd(OAc)_2/KOAc/[BzEt_3N]Cl$ in DMF as solvent, 25 °C, 10 d) is much more selective than the classical Heck catalyst system: 80 % **1**, 12 % **2** and only 8 % isomers are formed.

A twofold arylation both of the exocyclic and the endocyclic double bond does not take place under the reaction conditions described above neither with classical Heck's catalyst nor with Larock's catalyst. It was also shown in a separate experiment that **1** does not react further with the classical Heck catalyst ($Pd(OAc)_2/PPh_3/Et_3N$, 100 °C, 18 h). By using the more active P(*o*-tolyl)$_3$ instead of PPh_3, a formation of phenyl-(2-phenylvinyl)cyclohexenes was observed, but only in traces. Thus the endocyclic double bond in 4-vinylcyclohexene and in the phenylated derivative **1** is more inert than in cyclohexene which undergoes an allylic cross coupling under similar reaction conditions [1, 6, 10].

A twofold Heck reaction proceeds by using 4-vinylcyclohexene and *p*-diiodobenzene as substrates and Larock's phase-transfer catalyst system, cf. eq. 2. Similarly, a twofold Heck reaction between styrene and *p*-diiodobenzene was described using a classical catalyst system [11].



The longer the reaction time and the higher the concentration of $Pd(OAc)_2$ the more (*E,E*)-*p*-bis[2-(cyclohex-3-enyl)vinyl]benzene (**5**) is formed (tab. 1). The reaction proceeds via (*E*)-*p*-iodo-2-(cyclohex-3-enyl)vinylbenzene (**3d**, X'=I) as intermediate. *p*-Iodo-1-(cyclohex-3-enyl)vinylbenzene (**4d**, X'=I) and double bond isomers are formed as side products.

Table 1 Heck Arylation Reactions of 4-Vinylcyclohexene and *p*-Dihalobenzenes *p*-C_6H_6XX' (cf. eq. 2) at 25 °C.

X,X'	reaction time in d	[Pd] in mol-%	a)	product ratio (GC) in % b) 3	4	5	isomers
I,I	5	2.5	85	67	10	16	7
	13	2.5	92	61	10	21	8
	30	2.5	94	53	9	26	12
I,I	5	5	89	60 (12)	9	22	9
	5	25	96	39	5	39	17
	5	100	100	0	0	78	22
I,Br	13	2.5	96	84 (25)	12	0	4
I,Cl	5	2.5	100	80 (45)	10	0	10
I,F	5	2.5	100	81 (42)	13	0	6
Br,Br	2 c)	2.5	98	3	1	54 (37)	42

a) Consumption of *p*-diiodobenzene in %.
b) In parentheses: isolated yield in %.
c) Reaction temperature: 80 °C.

Starting with *p*-C_6H_4IX' (X'=F, Cl, Br) the monovinylated products **3** and **4** are the final products (tab. 1) in accordance with that only iodobenzenes undergo a Heck reaction with Larock's catalyst at room temperature [6]. But at 80 °C, Larock's catalyst system is also active with bromobenzenes: Thus 1.4-dibromobenzene reacts to give **5** in good yields (tab. 1).

The new hydrocarbons **3a–3b** (X'=F, Cl, Br, I) and **5** were isolated in a pure state by crystallization from cold *n*-pentane and were characterized by NMR (^{1}H, ^{13}C) and mass spectroscopy. The NMR spectra of compounds **3** are very similar to those of **1**. Differences are observed especially in the aromatic region and can be attributed to the influence of the halogen X'. The coupling constants $^nJ(^{19}F, ^{13}C)$ in **3a** agree very well with those in *p*-fluorostyrene [12]. The mass spectra of **3a–3d** have indicated in all cases the presence of the molecular ion $[M]^+$, followed by a retro Diels-Alder cleavage as main route to give $[M-54]^+$ as base peak in **3a**. In the case of **3b–3d**, a further fragmentation takes place under splitting off the halogen to give the base peak $[M-54-X]^+$.

Thus it can be stated that the endocyclic double bonds in 4-vinylcyclohexene and in the arylated derivatives **3** and **5** are less reactive against further arylation than in non-functionalized cyclohexene.

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Experimental

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Gemini 300 or a Bruker ACF 250 spectrometer. Chemical shifts (designed as C1 ... C6 in cyclohexenyl and as C1′, C2′ in vinyl groups) are reported in units of δ (ppm) relative to tetramethylsilane using $C\mathit{H}Cl_3$ (δ 7.24) and $\mathit{C}DCl_3$ (δ 77.00) as internal references. IR spectra were recorded on a Nicolet 205 spectrometer. GC analyses were performed on a Chrompack CP 9000 gas chromatograph equipped with a capillary column (25 m CP-SIL 19CB) and a flame ionization detector, nitrogen being used as a carrier gas. Mass spectra (electron impact, 70 eV) were recorded on a GC/MS unit (Hewlett Packard) equipped with a capillary column (30 m HP-5MS), helium being used as a carrier gas. Melting points are uncorrected. The reagents were purchased from commercial sources. DMF and DMSO were dried on 4Å molecular sieves and purified by vacuum destillation.

A Typical Procedure for the Heck Reaction

a) With $Pd(OAc)_2/PR_3/Et_3N$ as Catalyst System

5.0 mmol halo- or dihalobenzene, 2.70 g (25.0 mmol) 4-vinylcyclohexene, 0.25 mmol triphenylphosphine or tri-*o*-tolylphosphine and 0.028 g (0.125 mmol) $Pd(OAc)_2$ (2.5 mol-% relating to halobenzene) in 2.53 g (25.0 mmol) Et_3N were sealed under argon in an ampoule made from thick wall glass and stirred for 6 h at 100 °C. Ether (50 ml) was added, and the precipitated salts were filtered and washed with ether (2 × 50 ml). After solvent evaporation from the combined organic layer there was detected the degree of conversion gaschromatographically using durene as an internal standard.

b) With $Pd(OAc)_2/KOAc//[BzEt_3N]Cl$ as Catalyst System in DMF

5.0 mmol halo- or dihalobenzene, 5.41 g (50.0 mmol) 4-vinylcyclohexene, 1.47 g (15.0 mmol) KOAc, 1.14 g (5.0 mmol) $[BzEt_3N]Cl$ and 0.028 g (0.125 mmol) $Pd(OAc)_2$ (2.5 mol-% relating to halobenzene) in 20 ml DMF were stirred under argon at room temperature for 5–10 days. The reaction mixture was extracted with *n*-pentane or light petroleum (5 × 50 ml). After solvent evaporation from the combined organic layer, there was detected the degree of conversion gaschromatographically using durene as an internal standard.

c) Procedure for Hydrogenation of Reaction Mixture

The reaction mixture of the Heck reaction was extracted with *n*-pentane (5 × 25 ml). The combined pentane layer was filtered over silicagel 60 (10 g). After solvent evaporation the residue was dissolved in THF, and palladium (4 % on charcoal) was added. The hydrogenation was undertaken for 30 h (0.1 MPa hydrogen, 25 °C), small portions of fresh hydrogenation catalyst being added from time to time. Products were analyzed by using GC and GC/MS. *Reference substances:* 2-Cyclohexylethylbenzene (**1′**) was obtained by hydrogenation of **1**. The mass spectra (GC/MS) of **1′** and **2′** are in agreement with the data given in lit. [13]. 1-Ethyl-4-phenylcyclohexane was prepared by reacting 4-phenylcyclohexanone with EtMgBr and subsequent dehydratation and hydrogenation (analogous to lit. [14]). Mass spectrum: [*m/z* (%): 188 (44) [M^+], 118 (20), 117 (62), 104 (100), 91 (43), 78 (11), 55 (16), 41 (16)]. The mass spectrum (GC/MS) of 1-ethyl-3-phenylcyclohexane [*m/z* (%): 188 (70) [M^+], 159 (17), 145 (25), 131 (8), 117 (50), 104 (100), 91 (80), 81 (12), 78 (13), 55 (20), 41 (20)] corresponds to the mass spectrum of the methyl compound, which was prepared starting from 3-methylcyclohexanone quite analogously to the synthesis of 1-ethyl-4-phenylcyclohexane.

Preparation of (E)-2-(cyclohex-3-enyl)vinylbenzene (**1**)

40.80 g (0.20 mol) iodobenzene, 108.18 g (1.00 mol) 4-vinylcyclohexene, 32.71 g (0.33 mol) KOAc, 45.50 g (0.20 mol) $[BzEt_3N]Cl$ and 2.00 g (8.9 mmol) $Pd(OAc)_2$ were stirred in 420 ml DMF under argon for 10 days. Ether (1.2 l) was added, and the precipitated salts were filtered and washed with ether. After solvent evaporation and addition of water (300 ml), the residue was extracted with *n*-pentane (5 × 100 ml). The combined pentane layer was dried on $MgSO_4$. Solvent evaporation and flash chromatography (50 g silicagel 60; *n*-pentane as eluent) gave 45.9 g of a pale yellow oil (GC: 83 % **1**, 11 % **2**, 6 % isomers, 2 % iodobenzene). **1** crystallized from a solution of the crude product in 200 ml *n*-pentane at -78 °C (mp. < 0 °C). After recrystallization from *n*-pentane at -78 °C, **1** was obtained at room temperature as light yellow oil in a purity of 99 % (GC) in 42 % yield (15.1 g). $n_D^{20} = 1.5699$. ^1H-NMR: δ 1.40–2.49 (m, 7H; cycloaliphatic protons), 5.67, 5.68 (2H; cycloolefinic protons), 6.19 (dd, $^3J(H,H) = 15.97$ Hz, $^3J(H,H) = 6.82$ Hz, 1H; vinylic proton), 6.36 (d, $^3J(H,H) = 16.06$ Hz, 1H; vinylic proton), 7.14–7.33 (m, 5H; aromatic protons). ^{13}C-NMR: δ 24.78 (C5), 28.68 (C6), 31.34 (C2), 37.06 (C1), 125.91 (C_o), 127.92 (C1′), 128.41 (C_m), 135.62 (C2′), 137.76 (C_i), 126.78, 126.91 (C3, C4), C_p is not observed due to overlapping. IR (neat): ν 693 (vs), 746 (vs), 914 (m), 965 (vs), 998 (m), 1015 (m), 1072 (m), 1437 (s), 1449 (s), 1494 (s), 1573 (m), 1651 (m), 2836–3081 (br) cm^{-1}. MS: *m/z* (%) 184 (17) [M^+], 130 [M-54, 100; retro Diels-Alder cleavage], 115 (25), 104 (6), 91 (14), 80 (37), 51 (7).

n-Pentane was evaporated from the combined mother liquors. The residue contained about 60 % (GC) **2**, identified NMR and mass spectroscopically by comparison with an authentic sample (vide infra).

Preparation of 1-(cyclohex-3-enyl)vinylbenzene (2) as Reference Material

To 2.64 g (0.11 mol) sodium hydride in 60 ml DMSO (stirred under argon at 75–80 °C for 45 min) a solution of 44.47 g (0.11 mol) $[PPh_3Me]I$ in 150 ml DMSO was added at room temperature. The mixture was stirred for 10 min, and 20.49 g (0.11 mol) 4-cyclohexenylphenylketone in 20 ml DMSO were then added. After stirring for 90 min at room temperature and for 30 min at 60 °C, the reaction was quenched with water (150 ml). The reaction mixture was extracted with petrolether (4 × 200 ml), and the combined organic layer was dried on $MgSO_4$. Solvent evaporation and vacuum distillation ($bp._{11}$ 128–130 °C) gave 73 % (14.5 g) pure (96 % GC) **2** as a colourless oil. $n_D^{20} = 1.5545$. ^1H-NMR: δ 1.40–2.90 (m, 7H; cycloaliphatic protons), 5.12, 5.29 (2H; vinylic protons), 5.78, 5.79 (2H; cycloolefinic protons), 7.28–7.55 (m, 5H; aromatic protons). ^{13}C-NMR: δ 25.78 (C5), 28.07 (C6), 31.52 (C2), 38.27 (C1), 110.69 (C2′), 126.60 (C_o), 128.12 (C_m), 126.54, 126.71, 127.07 (C3, C4, C_p), 142.58, 154.03 (C_i, C1). MS: *m/z* (%) 184 (77) [M^+], 169 (18), 155 (83), 143 (60), 129 (100) [M-H-54; retro Diels-Alder cleavage], 115 (71), 91 (69), 77 (57).

Preparation of (E)-p-halo-2-(cyclohex-3-enyl)vinylbenzenes (3a–3d)

50.0 mmol *p*-haloiodobenzene (C_6H_4IX', X'=F, Cl, Br, I), 54.09 (500.0 mmol) 4-vinylcyclohexene, 14.72 g (150.0 mmol) KOAc, 11.37 g (50.0 mmol) $[BzEt_3N]Cl$ and 0.28 g (1.25 mmol) $Pd(OAc)_2$ were stirred in 200 ml DMF under argon (reaction time see table 1). After addition of water (100 ml) the reaction mixture was extracted with *n*-pentane (6 × 150 ml), and the combined organic layer was dried on $MgSO_4$. After solvent evaporation at reduced pressure the pure product was obtained by flash chromatography (80 g silicagel 60; *n*-pentane as eluent) and recrystallization from *n*-pentane at –78 °C.

3a (X'=F) [15]: 42 % yield; 98 % purity (GC); n_D^{27} = 1.5409. ^{1}H-NMR: δ 1.25–2.30 (m, 7H; cycloaliphatic protons), 5.62 (2H; cycloolefinic protons), 5.88 (dd, ^3J(H,H) = 15.93 Hz, ^3J(H,H) = 7.29 Hz, 1H; vinylic proton), 6.12 (d, ^3J(H,H) = 15.93 Hz, 1H; vinylic proton), 6.72 (dd, ^3J(H,H) = 8.67 Hz, 2H; aromatic protons), 6.93 (dd, ^3J(H,H) = 8.59 Hz, ^3J(F,H) = 5.52 Hz, 2H; aromatic protons). ^{13}C-NMR: δ 25.09 (C5), 29.07 (C6), 31.70 (C2), 37.38 (C1), 115.48 (d, ^2J(F,C) = 21.5 Hz; C_m), 127.85 (d, ^3J(F,C) = 7.7 Hz; C_o), 134.45 (d, ^4J(F,C) = 3.2 Hz; C_i), 135.40 (d, ^6J(F,C) = 2.1 Hz; C2'), 162.43 (d, ^1J(F,C) = 245.6 Hz; C_p), 126.21, 127.14, 127.48 (C3, C4, C1'). IR (NaCl): ν 657 (s), 808 (s), 847 (s), 967 (vs), 1087 (m), 1163 (s), 1220 (vs), 1488 (m), 1507 (vs), 1600 (s), 1652 (m), 1873 (w), 2833–3020 (br, s) cm^{-1}. MS: *m/z* (%) 203 (3) [M+1], 202 (17) [M$^+$], 159 (5), 148 (100) [M-54; retro Diels-Alder cleavage], 147 (62), 133 (27) [148-CH_3], 115 (7), 109 (12), 93 (3), 80 (19).

3b (X'=Cl) [15]: 45 % yield; 96 % purity (GC); mp. 35 °C. ^{1}H-NMR: δ 5.69 (2H; cycloolefinic protons), 6.18, 6.33 (2H, vinylic protons). ^{13}C-NMR: δ 127.00, 127.17, 128.54, 132.40 (C_i, C_o, C_m, C_p, C1'). IR (KBr): ν 656 (s), 807 (s), 975 (s), 1094 (s), 1487 (s) cm^{-1}. MS: *m/z* (%) 220 (5) [M+2], 218 (16) [M$^+$], 164 (32) [M-54; retro Diels-Alder cleavage], 129 (100) [M-54-Cl]. Anal. Calcd. for $C_{14}H_{15}Cl$: C, 76.88; H, 6.91. Found: C, 75.17; H, 7.05.

3c (X'=Br): 25 % yield; 98 % purity (GC); mp. 47–48 °C. ^{1}H-NMR: 5.69, 5.70 (2H; cycloolefinic protons), 6.20, 6.33 (2H; vinylic protons). ^{13}C-NMR: δ 120.45 (C_p). IR (KBr): ν 653 (vs), 803 (vs), 855 (vs), 971 (vs), 1008 (s), 1071 (s), 1486 (s) cm^{-1}. MS: *m/z* (%) 264/262 (6/6) [M$^+$ (^{81}Br/^{79}Br)], 210/208 (17/18) [M-54 (^{81}Br/^{79}Br); retro Diels-Alder cleavage], 129 (100) [M-54-Br]. Anal. Calcd. for $C_{14}H_{15}Br$: C, 63.89; H, 5.74; Br, 30.36. Found: C, 64.13, H, 6.13; Br, 29.29.

3d (X'=I): 12 % yield; 99 % purity (GC), mp. 43–45 °C. ^{1}H-NMR: δ 5.73, 5.74 (2H; cycloolefinic protons), 6.25, 6.34 (2H; vinylic protons). ^{13}C-NMR: δ 91.94 (C_p). IR (NaCl): ν 653 (vs), 742 (s), 799 (vs), 853 (vs), 967 (vs), 1003 (vs), 1059 (s), 1396 (s), 1433 (s), 1483 (vs), 1647 (s) cm^{-1}. MS: *m/z* (%) 310 (23) [M$^+$], 256 (48) [M-54; retro Diels-Alder cleavage], 129 (100) [M-54-I]. Anal. Calcd. for $C_{14}H_{15}I$: C, 54.21; H, 4.87. Found: C, 53.20; H, 5.29.

4d (X'=I) was characterized by GC/MS: *m/z* (%) 310 (100) [M$^+$], 282 (30), 281 (33), 269 (42), 268 (31), 244 (31), 231 (26), 183 (46), 167 (21), 154 (45), 142 (55), 129 (93) [M-54-I], 128 (96), 127 (38), 115 (36), 91 (19), 79 (50).

Preparation of (E,E)-p-bis[2-(cyclohex-3-enyl)vinyl]benzene (5)

a) From p-diiodobenzene and 4-vinylcyclohexene

1.65 g (5.0 mmol) *p*-diiodobenzene, 5.41 g (50.0 mmol) 4-vinylcyclohexene, 1.47 g (15.0 mmol) KOAc, 1.14 g (5.0 mmol) $[BzEt_3N]Cl$ and 1.40 g (6.24 mmol) $Pd(OAc)_2$ in 20 ml DMF were stirred under argon for 10 days at room temperature. After addition of water (100 ml), the reaction mixture was extracted with *n*-pentane (5 × 50 ml), and the combined organic layer was dried on $MgSO_4$. Solvent evaporation and flash chromatography (40 g silicagel 60; *n*-pentane as eluent) gave 1.13 g of a colourless oil (67 % **5**, GC). Recrystallization from *n*-pentane at –78 °C afforded 21 % (0.3 g) **5** in a pure state (99 % GC). mp. 77–77.5 °C. ^{1}H-NMR: δ 1.40–2.55 (m, 14H; cycloaliphatic protons), 5.73 (4H; cycloolefinic protons), 6.20 (dd, ^3J(H,H) = 15.93 Hz, ^3J(H,H) = 6.96 Hz, 2H; vinylic protons), 6.39 (d, ^3J(H,H) = 15.93 Hz, 2H; vinylic protons), 7.30 (s, 4H; aromatic protons). ^{13}C-NMR: δ 24.84 (C5), 28.78 (C6), 31.43 (C2), 37.13 (C1), 126.11 (C_o), 135.20 (C2'), 136.53 (C_i), 126.02, 126.94, 127.77 (C3, C4, C1'). IR (KBr): ν 533 (s), 654 (vs), 735 (s), 804 (vs), 862 (vs), 914 (s), 963 (vs), 1434 (s), 1452 (s), 2750–3050 (br) cm^{-1}. MS: *m/z* (%) 290 (64) [M$^+$], 236 (81) [M-54; retro Diels-Alder cleavage], 182 (100) [M-54-54; 2 × retro Diels-Alder cleavage], 167 (13), 141 (34), 128 (46), 44 (64). Anal. Calcd. for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 90.29; H, 8.97.

b) From p-dibromobenzene and 4-vinylcyclohexene

12.96 g (54.9 mmol) *p*-dibromobenzene, 29.17 g (274.6 mmol) 4-vinylcyclohexene, 0.308 g (1.37 mmol) $Pd(OAc)_2$, 12.50 g (54.9 mmol) $[BzEt_3N]Cl$ and 16.18 (164.8 mmol) KOAc were stirred in 110 ml DMF under argon for 2 days at 80 °C. The reaction mixture was worked up as described before. Yield: 5.93 g (37 %); 95 % purity (GC).

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