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A SHORT ROUTE TO DEHYDRO [12] ANNULENES.

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Abstract: A novel synthesis of dehydro [12] annulenes from 1,2-dibromobenzene is based on selective Pd(0)-Cu(1) coupling reactions of aryl and vinyl halides with terminal acetylenes.

The dehydroannulenes are a class of compounds having interesting properties.[1,2] They are usually prepared in low or modest yield by heating copper(I) acetylides with iodoarenes and iodoalkenes in boiling pyridine for several hours.[3,4]

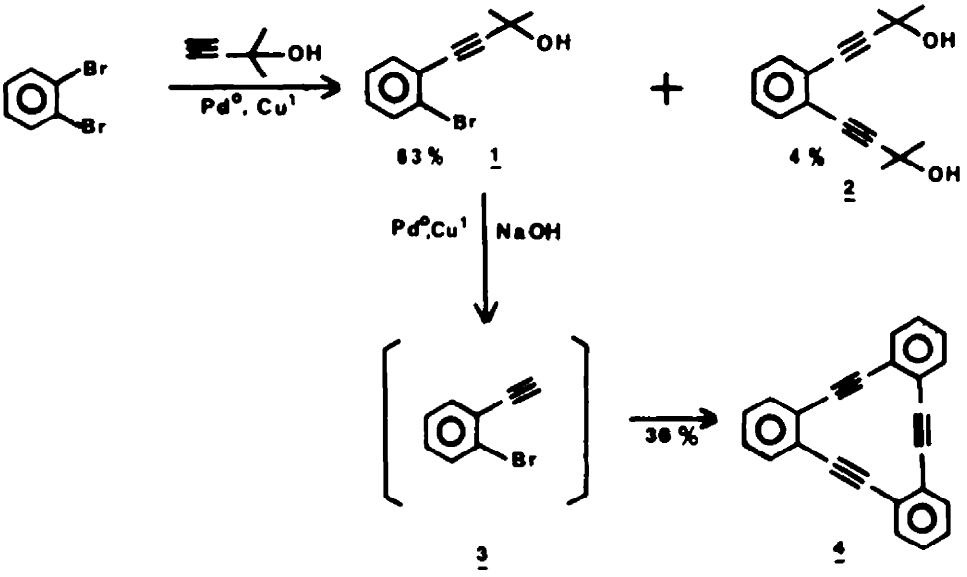
The palladium-copper catalysed reaction of acetylenes with aryl and vinyl halides provides an efficient synthesis of polyunsaturated compounds.[5,6,7] We now describe a synthesis of dehydro [12] annulenes by utilisation of this methodology which could be extended to the synthesis of other annulenes.

A two-step synthesis of 4 was based

(i) on the palladium-copper catalysed monosubstitution of 1,2-dibromobenzene by 2-methyl-3-butyn-2-ol in triethylamine.[8,9,10] 4 % of the disubstituted product 2 was easily separated by column chromatography.[11]

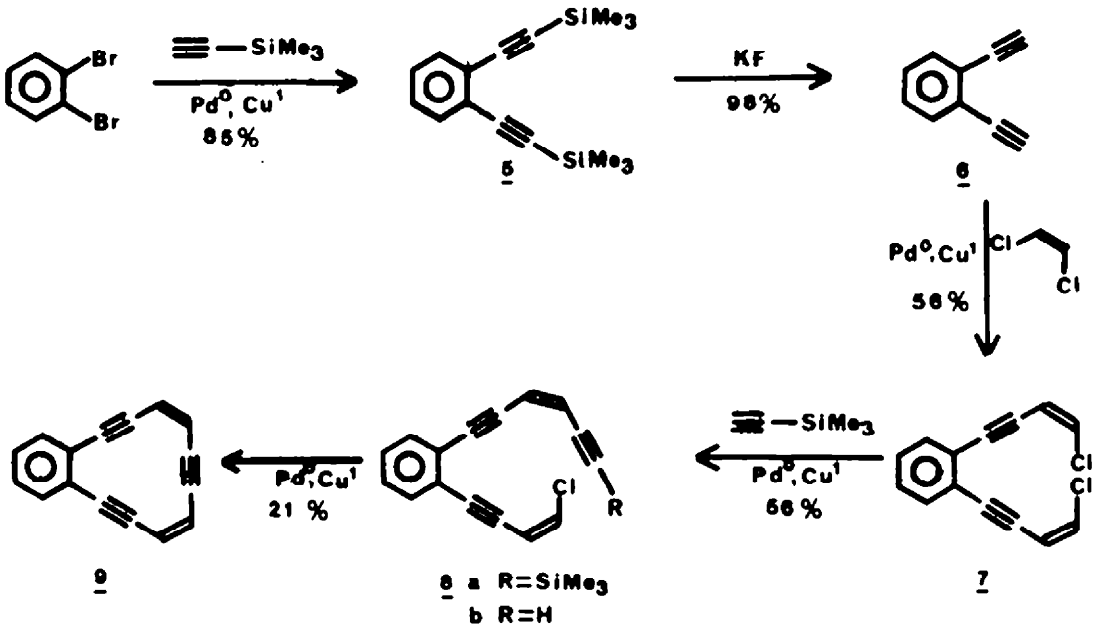
(ii) on the palladium-copper catalysed trimerisation of the bromoacetylene 3

Treatment of the alcohol 1 with aqueous sodium hydroxide and palladium-copper catalysts under phase-transfer conditions[12] generated the bromoacetylene 3 which trimerised in situ to give the tribenzoannulene 4 in 36 % yield.



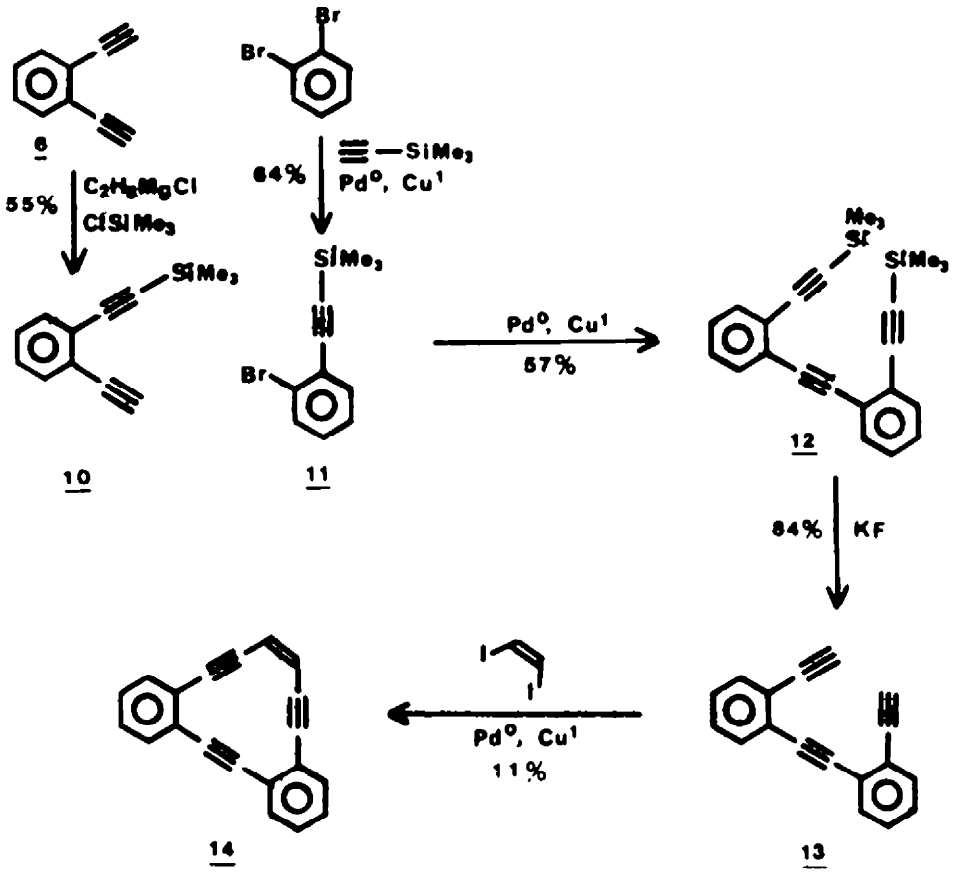
3 4

It was previously reported that (E) and (Z) enediynes can be prepared in high yield from (E) and (Z)-1,2-dichloroethylene.[6,7,11,12] This procedure was now extended to the synthesis of the dehydroannulenes 9 and 14.



The diacetylide 5 was prepared in 85 % yield from 1,2-dibromobenzene[15] and trimethylsilylacetylene (3 equiv.), in piperidine at 70°C. Desilylation with potassium fluoride-water in dimethylformamide gave 1,2-diethynylbenzene 6 in 98 % yield. Treatment with (Z)-1,2-dichloroethylene afforded 56 % of (Z)-chloroenyne 7.

We expected to obtain directly the dehydroannulene 9 by reaction of acetylene with 7 under palladium-copper catalysis. However, this reaction failed. 9 was prepared as follows : treatment of the dichloride 7 with trimethylsilylacetylene gave 56 % of 8a . Desilylation (78 %) and treatment under palladium-copper catalysis in benzene at room temperature for 16h led to 9[16] in 21 % yield.



The dehydroannulene 14 was synthesized by a similar sequence : the bromo compound 11 was prepared (64 %) by monosubstitution of 1,2-dibromobenzene (1 equiv.) with trimethylsilylacetylene (2 equiv.) in triethylamine at 70° in the presence of the palladium-copper catalysts. 3.5% of the disubstituted product 5 was separated by distillation. The monosilylated compound 10 was obtained in 55 % yield from 1,2-diethylnyl benzene 6 (1 equiv.) when treated with ethylmagnesium bromide (1.1 equiv.) and then trimethylchlorosilane (1.5 equiv.). Coupling of the two compounds 10 and 11 under palladium-copper catalysis (4h at 80°C) gave (57 %) the silylated triene 12 which was desilylated with potassium fluoride to afford (84 %) the triyne 13 [4,17] Treatment of 13 with (Z)-1,2-dichloroethylene in the presence of the palladium-copper catalysts gave the dichloride 15[18] instead of the expected cyclic product 14.[4] This product was finally obtained (11 %) when treated with (Z)-1,2-diiodoethylene in benzene at room temperature for 20h.

EXPERIMENTAL

All coupling reactions were carried out under an atmosphere of argon with dry freshly distilled solvents under anhydrous conditions. Boiling and melting points are uncorrected. The purity of the described products has been checked by thin layer chromatography (silica gel 60F-254 Merck). G.L.C. analyses were performed using an Intersmat model IGC 120 FL on a OV 17 % glass-packed column 1.5m.
The ^1H NMR spectra were recorded on a Cameca 250 Spectrometer ; ^1H chemical shifts are given in d (ppm) from internal TMS. The ^{13}C NMR spectra were recorded on a Brucker WH 90 MHz and a Brucker AL 100 MHz spectrometer. ^{13}C chemical shifts are given in d (ppm) from TMS with the solvent peaks as internal standard. I.R. spectra were recorded with a Perkin Elmer model 397 spectrometer.
The mass spectra were recorded on a Nermag R10-10B spectrometer, with electronic impact 70 ev (E.I.) or chemical ionisation with NH_3 (C.I.).

Palladium-copper catalysed preparation of 1 :
2-methyl-3-butyn-2-ol (5.04 g, 60 mmol) and copper(I) iodide (0.61g, 3.2 mmol) are added at 60°C to a stirred suspension of tetrakis(triphenylphosphine)palladium[19] (1.84g, 1.6 mmol) and 1,2-dibromobenzene (9.44g, 40 mmol) in triethylamine (100 ml). The mixture is stirred at 60°C for 5h. The amine is removed in vacuo, and a saturated aqueous ammonium chloride solution (60 ml) is added. After extraction with ether (2x100 ml), the organic phase is washed with water (100 ml) and dried over magnesium sulfate. The solvent is removed in vacuo, and the crude product is purified by chromatography on silicagel (300g).
Elution with pentane gives unreacted 1,2-dibromobenzene (1.40g) ;
elution with ether/pentane (20/80) gives the bromo arylalkynol 1 as a nearly colourless oil ; yield : 6.03g (63 %) :
$C_{11}H_{11}BrO$ (239.12) calc. : C 55.25 ; H 4.64 ; Br 33.42 found : C 55.40 ; H 4.68 ; Br 33.31
M.S. : m/e = 240 (M^+, ^{81}Br), 238 (M^+, ^{79}Br).IR (neat) : n = 3360, 2230 cm^{-1}.
^1H-NMR (80 Mz, $CDCl_3$/TMS) : d = 1.63 (s, 6) ; 2.72 (br.s, 1H); 6.92-7.22 (m, 2H); 7.22-7.47 ppm(m, 2H).
^{13}C-NMR ($CDCl_3$) : d = 31.25 ; 65.66 ; 80.80 ; 98.44 ; 124.74 ; 125.63 ; 126.90 ; 129.36 ; 132.27 ; 133.16 ppm. Elution with ether/pentane (50:50) gives 2 which is recristallized from isopropyl ether ; yield: 0.38g (4 %) ; m.p. 73°C. $C_{16}H_{18}O_2$ (242.32) calc. C 79.30 ; H 7.49found C 79.18 ; H 7.39 M.S. : m/e = 242 (M^+). IR (KBr) : n = 3360, 2200 cm^{-1}. ^1H-NMR (80 MHz, $CDCl_3$/TMS) : d = 1.62 (s, 12H) ; 2.98 (br.s, 2H) ; 7.0-7.37ppm (m, 4H). ^{13}C-NMR ($CDCl_3$) : d = 31.40 ; 65.60 ; 80.78 ; 98.13 ; 125.48 ; 127.74 ; 131.20 ppm.

Palladium catalysed preparation of 1 :
2-Methyl-3-butyn-2-ol (0.63g, 7.5 mmol) is added at 80°C to a stirred suspension of tetrakis (triphenylphosphine) palladium (0.115g, O.1 mmol) and 1,2-dibromobenzene (1.16g, 5 mmol) in piperidine (15 ml). The mixture is stirred at 80°C for 9h. After treatment as above, the crude product is purified by chromatography on silicagel (80g). Elution with pentane gives unreacted 1,2-dibromobenzene (0.42 g) ; elution with ether/pentane (20/80) gives 1, yield : 0.61g (51 %).

5,6,11,12,17,18-Hexadehydro-tribenzo [a,e,i] cyclododecene 4 :
5N aqueous solution of sodium hydroxide (3 ml) is added to a stirred mixture of bromo arylalkynol (1 ; 0.72g, 3 mmol), tetrakis-(triphenylphosphine)palladium (0.16g, 0.14 mmol), copper(I) iodide (0.O3g, 0.14 mmol), and benzyltriethylammonium chloride (0.03g, 0.11 mmol) in benzene (8 ml). The mixture is stirred at 85°C for 22h and then allowed to room temperature. After quenching with aqueous ammonium chloride (20 ml) and extraction with benzene (50 ml), the organic phase is dried over magnesium sulfate. The solvent is evaporated in vacuo, and the crude product is purified by chromatography on silica gel [40g, eluent methylene chloride/pentane (20:80)]. Crystallisation from isopropyl ether/pentane gives yellow crystals of 4[3,4]; yield : 0.11g (36%); m.p. 210°C. M.S. : m/e = 300 (M^+)I.R. (KBr) : n = 2225 cm^{-1}. ^1H-NMR (80 MHz, $CDCl_3$/TMS) : d = 6.90-7.32 ppm (m, 12H). ^{13}C-NMR ($CDCl_3$) : d = 92.90 ; 126.78 ; 128.45 ; 131.98 ppm.

1,2-Diethynyl benzene 6 :

A solution of 1,2-di(trimethylsilylethynyl) benzene[15] (5, 14g, 52 mmol), potassium fluoride (4.53g, 78 mmol) and water (4 ml) in dimethylformamide (150 ml) is stirred at room temperature for 4h. The mixture is poured on to ice (100 g). The product is extracted with methylene chloride (2x100 ml), washed with water (4x100 ml), dried over magnesium sulfate. After evaporation of the solvent in vacuo, the product is distilled through a 12 cm vigreux column to give 1,2-diethynylbenzene 6 as a colorless oil[3] ; yield : 6.48g (98 %) ; b.p. 32-35°C/0.5 torr.M.S. : m/e = 126 (M^+)I.R. (neat) : n = 2120 cm^{-1}. ^{1}H-NMR (80 MHz, $CDCl_3$/TMS) : d = 3.15 (s, 2H) ; 6.95-7.40 ppm (m, 4H). ^{13}C-NMR ($CDCl_3$) : d = 81.21 ; 81.69 ; 124.35 ; 128.38 ; 132.46 ppm.

Chloroenyne 7 :

A mixture of (Z) 1,2-dichloroethylene (6.37g, 66.4 mmol) and tetrakis (triphenylphosphine) palladium (1.15g, 1 mmol) in benzene (50 ml) is stirred at room temperature for 30 mn. 1,2-Diethynylbenzene (6 ; 2.1g, 16.6 mmol), n-butylamine (3.65g, 50 mmol) and copper(I) iodide (0.285g, 1.5 mmol) are added. The temperature rises from 20°C to 25°C. After stirring for 2h at 22°C, the mixture is hydrolyzed with water (40 ml), and extracted with ether (2x40 ml). The organic extract is dried over magnesium sulfate, and evaporated in vacuo. The residue is filtrated through silicagel (100g, elution with pentane) and gives 7 (yellowish oil) ; yield : 2.29g (56 %).

$C_{14}H_8Cl_2$ (247.13) Calc. C 68.05 ; H 3.26 ; Cl 28.69 found C 68.70; H 3.0 ; Cl 28.3 M.S. : m/e = 250 (M^+, $^{37}Cl^{37}Cl$) ; 248 (M^+,$^{37}Cl^{35}Cl$) ; 246 (M^+, $^{35}Cl^{35}Cl$) I.R. (neat) : n= 2200 cm^{-1}. ^{1}H-NMR (80 MHz, $CDCl_3$/TMS) : d = 6.0 (d, 2H, J=7Hz) ; 6.3 (d, 2H, J=7Hz) ; 7.02-7.50 ppm (m, 4H). ^{13}C-NMR ($CDCl_3$) : 87.29 ; 95.87 ; 112.11 ; 125.11 ; 128.41 ; 128.63 ; 132.09 ppm.

Chloroenyne 8a :

To a stirred mixture of 7 (0.90g, 3.6 mmol) and tetrakis (triphenylphosphine) palladium (0.18g, 0.15 mmol) in benzene (20 ml) are added trimethylsilylacetylene (0.44g, 4.50 mmol), n-butylamine (0.40g, 5.5 mmol) and copper(I) iodide (0.06g, 0.3 mmol). After stirring for 16h at room temperature and working up in usual manner, the residue is flash-chromatographed on silicagel. Elution with pentane gives 8a as a yellowish oil ; yield : 0.62g (56 %).

$C_{19}H_{17}ClSi$ (308.89) Calc C 73.88 ; H 5.55 ; Cl 11.483.0 Found C 74.20 H 5.70 ; Cl 10.80. M.S: m/e = 310 (M^+,^{37}Cl) ; 308 (M^+,^{35}Cl) I.R. (neat) : n = 2200, 2150 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$/TMS) : d = 0.22 (s, 9H) ; 5.94 (d, 1H, J=11Hz) ; 6.16 (d, 1H, J=11Hz) ; 6.18 (d, 1H, J=7Hz) ; 6.48 (d, 1H, J=7Hz) ; 7.40-7.28 (m,2H) ; 7.50-7?60 ppm (m, 2H). ^{13}C-NMR ($CDCl_3$) : -0.20 ; 87.29 ; 91.01 ; 95?74 ; 95.81 ; 102.15 ; 103.46 ; 112.10 ; 119.25 ; 120.60 ; 125.03 ; 125.49 ; 128.27 ; 128.35 ; 128.87 ; 132.05 ; 132.22 ppm.

Chloroenyne 8b :

A solution of 8a (0.50g, 1.62 mmol), potassium fluoride (0.28g, 4.82 mmol) and water (0.5 ml) in dimethylformamide (5 ml) is stirred at room temperature for 4h. The mixture is poured onto ice (5g), extracted with methylenechloride (2x30 ml), washed with water (4x30 ml) and dried over magnesium sulfate. After evaporation of the solvent in vacuo, the residue is purified by chromatography on silicagel.

Elution with pentane gives 8b (yellowish oil), yield : 0.30g (78 %).

$C_{16}H_9Cl$ (236.70) Calc. C 81.19 ; H 3.8Found C 81.50 ; H 3.75 M.S. : m/e = 238 (M^+,^{37}Cl) ; 236 (M^+,^{35}Cl) I.R. (neat) : n = 3300, 2180, 2130 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$/TMS) : d = 3.42 (dd, H, J=2.5Hz, J=0.5Hz) ; .5.92 (dd, 1H, J=11.5Hz, J=2.5Hz) ; 6.20 (d,1H, J=7.5Hz) ; 6.24 (dd, 1H, J=11.5Hz, J=0.5Hz) ; 6.52 (d, 1H, J=7.5Hz) ; 7.28-7.42 (m, 2H) ; 7.52-7.62 ppm (m,2H). ^{13}C-NMR ($CDCl_3$) : d = 80.78 ; 85.20 ; 87.29 ; 90.43 ; 95.75 ; 95.81 ; 112.22: 118.52 (2c) ; 121.56 ; 125.17 ; 125.29 ; 128.43 ; 128.65 ; 132.16 ; 132.40 ppm.

5,6,9,10,13,14-Hexadehydrobenzocyclododecane 9 :
To a mixture of tetrakis (triphenylphosphine) palladium (0.18g, 0.15mmol) and 8b (0.45g, 1.9 mmol) in benzene (10 ml) are added sequentially with stirring at room temperature n-butylamine (0.21g, 2.9mmol) and copper(I) iodide (0.03g, 0.15 mmol). After stirring for 16h, a saturated aqueous solution of ammonium chloride (10 ml) is added. After extraction with ether (2x30 ml), the organic layer is dried over magnesium sulfate. The solvent is then evaporated in vacuo, the residue is purified by chromatography on silica gel (10g, elution pentane). The orange cristals of 9^{12} are crystallised from pentane, yield : 0.08g (21%); m.p. 94-95°C. M.S. : m/e = 200 (M^+). I.R. (KBr) : n = 2180, 2160 cm^{-1}. U.V. (C_2H_5OH) : l_{max} (e) = 250 (36.000) ; 265 (38.600) ; 271 (40.000) ; 280 (85.600) nm. ^{1}H-NMR (250 MHz, $CDCl_3$/TMS) : d = 5.0 (d, 4H, J=8.5Hz) ; 6.50-6.60 (m,2H) ; 6.6-7.62 ppm (m, 2H). ^{13}C-NMR ($CDCl_3$) : d = 92.46 ; 96.95 ; 97.72 ; 121.93 ; 123.16 ; 128.06 ; 129.37 ; 132.16 ppm.

Preparation of 10 :
Ethylmagnesium bromide in tetrahydrofuran (38 ml, 60 mmol) is added dropwise with stirring, at 5°C, to 1,2-diethynylbenzene 6 (6.30g, 50mmol) in tetrahydrofuran (40 ml). The cooling bath is then removed and the stirred solution is allowed to reach 20°C, and kept 1.5h at this temperature. Trimethylchlorosilane (8.1g, 75 mmol) is added at 0°C. The mixture is stirred for 1.5h at room temperature, then quenched with water (110 ml) at 0°C and extracted with ether (100 ml). The organic layer is washed with ammonium chloride solution (2x50 ml) and dried over magnesium sulfate.
Evaporation of the solvent and distillation through a 15 cm Vigreux column gives a) 1,2-diethynylbenzene 6 (0.82g) b.p. 40°C/0.1 torr.
b) 10 as a colourless oil ; yield : 6?46g (55 %) ; b.p. 80-82°C/0.1 torr.
$C_{13}H_{14}Si$ (198.34) calc. C 78.72 ; H 7.11 ; found C 78.60 ; H 7.05.
M.S. : m/e = 198 (M^+). I.R. (film) : n = 3300, 2180, 2120 cm^{-1}. ^{1}H-NMR (80 MHz, $CDCl_3$/TMS) : d = 0.18 (s, 9H) ; 3.12 (s, 1H) ; 6.90-7.40ppm (m, 4H).
^{13}C-NMR ($CDCl_3$) : d = 81.10 ; 81.92 ; 98.37 ; 103.02 ; 125.00 ; 126.07 ; 128.08 ; 128.34 ; 132.00 ; 132.35 ppm.
c) 5 as a colourless oil ; yield : 0.33g (20 %) ; b.p. 100°C/0.1 torr, m.p. 50°C.

Preparation of 11 :
To a stirred solution of 1,2-dibromobenzene (11.8g, 50 mmol), in triethylamine (150 ml), trimethylsilylacetylene (9.7g, 100 mmol) tetrakis (triphenylphosphine) palladium (2.3g, 2 mmol) and copper(I) iodide (0.76g, 4 mmol) are added. The mixture is heated for 7h at 70°C. After cooling the triethylamine is removed in vacuo. Ether is added, the organic phase is washed with water (2x200 ml), dried over magnesium sulfate. After evaporation of the solvent, the crude product is fractionated through a 15 cm Vigreux column to give successively :
a) 11 as a colorless oil ; yield : 8.00g (64 %) ; b.p. 85°C/0.1 torr.
$C_{11}H_{13}BrSi$ (253.2) calc. C 52.18 ; H 5.17 ; Br 31.56 found C 51.93 ; H 5.10 ; Br 31.90.
M.S. : m/e = 254 (M^+, ^{81}Br) ; 252 (M^+, ^{79}Br). I.R. (neat) : n = 2160 cm^{-1}. ^{1}H-NMR ($CDCl_3$/TMS) : d = 0.30 (s, 9H) ; 6.82-7.20 (m, 2H) ; 7.2-7.5 ppm (m, 2H). ^{13}C-NMR ($CDCl_3$) : d = -0.18 ; 99.60 ; 103.00 ; 125.22 ; 125.73 ; 126.85 ; 129.52 ; 132.33 ; 133.56 ppm.
b) 5 ; yield : 0.48g (3.5 %) ; b.p. 100°C/0.1 torr ; m.p. 50°C.

Preparation of the triyne 12 :
A solution of 11 (1.92g, 7.62 mmol) and tetrakis (triphenylphosphine) palladium (0.35g, 0.3 mmol) in triethylamine (25 ml) is heated at 80°C. To this solution are added the acetylenic compound 10 (1.50g, 7.57 mmol) and copper(I) iodide (0.08g, 0.4 mmol). The mixture is heated for 4h at 80°C. Triethylamine is removed in vacuo, and water (20 ml) is added. After extraction with ether (2x50 ml), the organic extracts are washed with water (50 ml) and dried over magnesium sulfate. The solvent is removed in vacuo and the crude product is purified by chromatography on silicagel (100g). Elution with pentane gives 12 which is crystallised from ether/pentane : yield : 1.60g (57 %) ; m.p. 118-120°C. $C_{24}H_{26}Si_2$ (370[illegible]) C 77.77 ; H 7.08 Found C 77.62 ; H 7.10
M.S. : m/e = 370 (M^+).I.R. (KBr) : n = 2160 cm^{-1}. ^{1}H-NMR (80 MHz, $CDCl_3$/TMS) = d = 0.28 (s, 18H) ; 7.05-7.62 ppm (m, 8H). ^{13}C-NMR ($CDCl_3$) : -0.03 ; 92.09 ; 98.83 ; 103.44 ; 125.56 ; 126.11 ; 127.96; 128.07 ; 131.88 ; 132.14 ppm.

Preparation of the triyne 13 :
A solution of the triyne 12 (0.8g, 2.16 mmol), potassium fluoride (0.5g, 8.6 mmol) and water (0.1 ml) in dimethylformamide (15 ml) is stirred at room temperature for 4h. The mixture is poured over ice (20g). The product is extracted with methylene chloride (2x30 ml), washed with water (4x40 ml), dried over magnesium sulfate. After evaporation of the solvent in vacuo, the residue is crystallised from pentane ; yield : 0.44g (84 %) ; m.p. 75-76°C. (Lit.[4] m.p. 73-75°C).
$C_{18}H_{10}$ (226.28)Calc. C 95.55 ; H 4.45 Found C 95.60 ; H 4.40.
M.S. : m/e = 226 (M^+). I.R. (KBr) : n = 3280, 2150, 2100 cm^{-1}. ^{1}H-NMR (80 MHz, $CDCl_3$/TMS) : d = 3.30 (s, 2H) ; 7.10-7.55 ppm (m, 8H). ^{13}C-NMR ($CDCl_3$) : d = 81.38 ; 82.10 ; 91.89 ; 124.41 ; 126.08 ; 128.13 ; 128.47 ; 132.23 ; 132.56 ppm.

5,6,11,12,15,16-Hexadehydro-dibenzo [a,e] cyclododecene 14 :
(Z) 1,2-diiodo ethylene[4] (0.28g, 1 mmol) and n-butylamine (0.22g, 3 mmol) in benzene (8 ml) are added at room temperature to a mixture of tetrakis (triphenylphosphine) palladium (0.12g, 0.1 mmol), copper iodide (0.019g, 0.1 mmol) and 2,2-diethynyldiphenylacetylene 13 (0.23g, 1 mmol) in benzene (5 ml). After 20h, the reaction is quenched with water, extracted with ether (2x50 ml), and the organic layer is dried over magnesium sulfate. The crude product, obtained after evaporation of the solvent in vacuo is purified by filtration through a silica gel column (20g, pentane as eluent) and then crystallised from pentane to give yellow crystals of 14[4] ; yield : 0.03g (11 %) ; m.p. 112°C. M.S. : m/e = 250 (M^+). I.R. (KBr) : n = 2220, 2200 cm^{-1}. ^{1}H-NMR (80 MHz, $CDCl_3$/TMS) : d = 5.52 (s, 2H); 6.80-7.15 (m,8H) ppm. ^{13}C-NMR ($CDCl_3$) : d = 92.47 ; 92.88 ; 97.39 ; 121.57 ; 126.83 ; 127.59 ; 128.69 ; 128.98 ; 131.87 ; 132.19 ppm.

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8. Under the same conditions, by using an unencumbered amine such as piperidine, 1 and 2 wereobtained in 56 % and 31 % respectively ; however, by using 3 equiv. (instead of 1.5 equiv.) of 2-methyl-3-butyn-2-ol, the diol 2 was obtained in 82 % yield.

9. Under Pd-Cu conditions, when the reaction was performed at 22 % for 24h in triethylamine, piperidine or propylamine, by using 2-methyl-3-butyn-2-ol in excess (3 equiv.), the monosubstituted product 1 was obtained in 25 % yield. The disubstituted product 2 was not formed.

10. The step wise reaction of 1,2-dibromobenzene with acetylenes has been recently reported : G. Just, and R. Singh. Tetrahedron Lett., 1987, 28, 5981.

11. Without copper iodide, the formation of 1 was not observed. However, when 1,2-dibromobenzene was treated with 2-methyl-3-butyn-2-ol (1.5 equiv.) and $Pd(PPh_3)_4$ (2 %), without copper iodide, in piperidine at 80°C for 9h, the bromoalcohol 1 was isolated in 51 % yield.[16]

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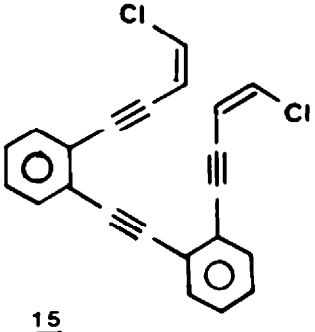
18. 

15

m.p. 85-87°C.

$C_{22}H_{12}Cl_2$ calc.C 76.10H 3.48

(347.25) found 76.10 3.62

M.S. : m/e = 350, 348, 346

I.R. (KBr) : n 2220, 2200 cm^{-1}

^{1}H-NMR (80MHz, $CDCl_3$/TMS) :

d = 6.03 (d, 2H, J=7Hz);

6.35 (d, 2H, J=7Hz) ; 7.10-7.62 ppm

(m,8H). ^{13}C-NMR ($CDCl_3$) : d = 87.16 ;

92.06 ; 96.04 ; 112.19 ; 125.17 ; 125.64 ;

128.10 ; 128.38 ; 128.58 ; 132.11 ;

132.34ppm.

19. Y.S. Vavshavskii and N.V. Kiseleva, Chemical Abstracts, 1974, 80, 12897 V.