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Synthesis Of 1,10-Dichlorobenzo[C]Cinnoline, And Its N-Oxide With Some Strained Molecules Related To Biphenylene.

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ABSTRACT

The 1, 10- dichlorobenzo[c]cinnoline (3)was synthesised in three steps, from the commercially available 1,2- dichloro-3-nitrobenzene (1), the oxidation of (3) with hydrogen peroxide in acetic acid gave the 1, 10- dichlorobenzo [c] cinnoline –5- oxide (4). Vacuum pyrolysis of the cinnoline (3) at 800 °C, gave pure 1,8-dichlorobiphenylene (5) in high yield, and the latter hydrocarbon (5) is an intermediate molecule in order to synthesise some polycyclic aromatic hydrocarbons related to biphenylene such as cyclo-octatetraene derivative (10a).

Keywords: Dichlorobenzo[c]cinnoline, dichlorobiphenylene, biphenylene, cyclo-octatetraene derivative.

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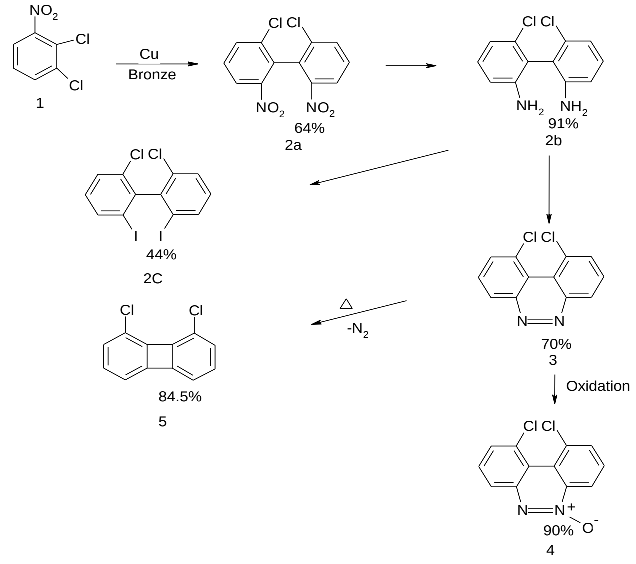
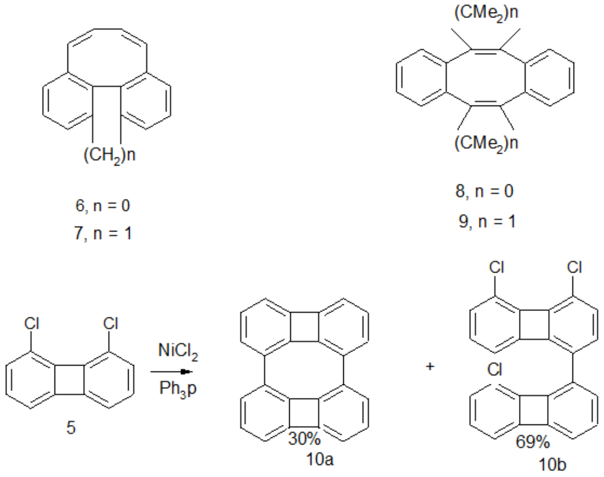
INTRODUCTION

According to Hückels (4n + 2) л- electron rule a planar [8] annulene should be anti-aromatic and would be expected to sustain paramagnetic ring current. The simplest [8] annulene, cyclo-octatetraene (COT), is non – planar and its properties are similar to those of an open –chain. In this connection, several derivatives of cyclo-octatetraene such as (6), (7),[1] (8) and (9),[2] in which the 8-membered ring is forced to be planar, have been synthesized. These show the effects of very strong paramagnetic ring current in their nmr spectra. [1, 2]



Scheme I

The biphenylene ring system contains a rigid group of four carbon atoms (1,8, 8a, and 8b) and if two biphenylene molecules could be joined at the 1, 1’- and 8, 8’-position, they would give a rigid, planar polycyclic systems (10a) which formally contains a planar COT as well as two cyclobutadiene systems, the compound (10a) would be expected to show a very large paramagnetic ring current. We record here the synthesis of many new derivatives related to biphenylene, including the title compound (4).



Scheme II

EXPERIMENTAL SECTION

Unless other wise stated, the following conditions apply, (MS) Spectra were determined on an AET MS9 instrument updated with VG ZAB components. (IR) Spectra were recorded on a Perkin-Elmer 1420 Spectrophotometer. ^{1}H nmr Spectra were recorded on a jeol Gx270 as a solution in $CDCl_3$ with TMS as an internal standard; (TLC), using Silica plates, was employed for examination of reaction mixture during and after each reaction. Column chromatography was carried out on Silica gel (60-120 mesh; BHD); Kieselgel (Mark 60H) or aluminum oxide (BDH). Petroleum refers to light petroleum (bp 60-80 °C). Elemental microanalyse were performed in the school of chemistry microanalytical laboratory, Bristol (UK).

2,2`-Dichloro-6,6`-dinitrobiphenyl (2a). 1,2-dichloro-3-nitrobenzene (20g, 104.2mmol) was heated at 250°C (silicon oil bath) while copper bronze (14g) was added in small portions in the usual way (total time ca30 min). The reaction mixture was kept at 250-260°C for a further 30 min, cooled, extracted, with boiling acetone, and filtered. The filtrate was evaporated, and the crude product was recrystallised from ethanol (using charcoal) to give the dinitro-compound (2a) (10.4g, 64%) as brown crystals, mp 171-172 °C.

^{1}H NMR, δ 7.81 (2H,dd, H-3/H-3`), 7.59 (2H,t, H-4/H-4`) and 8.21 (2H, dd, H-5/H-5`), $J_{3,4}$=7.48Hz, $J_{3,5}$=0.64Hz and $J_{4.5}$=7.48Hz. MS m/z 312(7,M^+), 266(100, M^+-NO_2). Anal. Found : C, 45.95 ; H, 1.93; Cl, 23.54 ; N, 8.76. Calcd for $C_{12}H_6Cl_2N_2O_4$: C, 46.03 ; H, 1.93 ; Cl, 22.65 ; N, 8.95.

2,2`-Diamino-6,6`-dichlorobiphenyl (2b)

(a) Using stannous chloride. A solution of (2a) (1g, 3.19 mmol) was warmed on the water-bath with tin (II) chloride dihydrate (5g) in ethanol (15 mL) and conc HCl (10 mL) for 1hr. the cooled solution was rendered alkaline with dilute aqueous NaOH, and the crude product was collected by ether extraction. After removal of the solvent, recrystallisation of the residue from ethanol gave the diamine (2b) (0.68g, 72 %) as pink prisms, mp 202-203°C.

^{1}H NMR, δ 6.71 (2H,d, H-3/H-3`), 7.14 (2H,t, H-4/H-4`), 6.92 (2H, dd, H-5/H-5`) and 2.99 (4H, br, 2NH_2), $J_{3,4}$=7.90Hz, $J_{3,5}$=1Hz and $J_{4,5}$=7.90Hz. MS m/z 252(51, M^+), 216(100), 181(13). Anal Found: C, 56.63 ; H, 4.08 ; Cl, 29.70 ; N, 10.94. Calcd for $C_{12}H_{10}Cl_2N_2$: C, 56.94; H, 3.98 ; Cl, 28.01 ; N,11.06 %.

(b) Using Raney nickel. 2,2`-Dichloro-6,6`-dinitrobiphenyl (2a) (3.13g, 10.0 mmol) in hot ethanol (80mL) was treated with hydrazine hydrate (4 mL), then Raney nickel in small portions until the vigorous reaction subsided. After being heated on the water-bath under reflux for 30min, the solution was filtered and the filtrate was concentrated to give the diamine (2b) (2.3g, 91%), mp 202-203°C.

Some similar experiments gave a mixture of the diamine (2b) and 1,10-dichlorobenzo [c] cinnoline (3). In these cases the crude product was warmed with dilute aqueous hydrochloric acid (1:9 concentrated acid: water); cooled, and filtered. The filtrate was treated with activated charcoal and neutralised with ammonia to give the diamine; from the mother-liquor was obtained 1,10-dichlorobenzo [c] cinnoline (3) as deep orange needles (from ethanol), mp 112-114 °C.

1,10-Dichlorobenzo [c] cinnoline (3). The diamino compound (2b) (1.15g, 4.54 mmol) in dry benzene (60 mL) was treated with phenyliodosodiacetate (3.25g, 10.41mmol), the reaction mixture being kept for 2 days at room-temperature under nitrogen. The filtrate was washed with 5% sodium carbonate solution, dried over magnesium sulphate, and evaporated under reduced pressure. Chromatography of the residue on alumina with benzene as eluent gave the cinnoline (3) (0.79g, 70%) as deep orange needles, mp 112-114°C.

^{1}H NMR, δ 7.94 (2H,dd, H-3/H-8), 7.86 (2H,t, H-4/H-7) and 8.46 (2H, dd, H-5/H-6), $J_{3,4}$=7.91Hz, $J_{3,5}$=1.5Hz and $J_{4,5}$=7.91Hz. MS m/z 248 (62, M^+), 220 (100, M^+ - N_2), 185(29), 149(19), 150(90). Anal. Found : C, 57.81 ; H, 2.34 ; Cl, 28.60 ; N, 11.28. Calcd for $C_{12}H_6Cl_2N_2$: C, 57.86 ; H, 2.43 ; Cl,28.46 ; N, 11.25%.

1,10–Dichlorobenzo[c]cinnoline -5-oxide (4) 1,10–dichlorobenzo[c]cinnoline (3), (0.200 g, 0.80 mmol) was dissolved in 6 ml of acetic acid and 1 ml of hydrogenperoxide (H_2O_2). The mixture was heated and stirred at 80 °C for 8 hr (using a water-bath) when the solid was formed, then the mixture was cooled, filtered ,the wet solid which was obtained, dried well and recrystallised from benzene, give the required product (4), yielding (0.180 g, 90 %) as a pale yellow prisme crystals, m.p. 101 – 102 °C.

Mass spectrum m/z (%) 264, 266 (56, 37, M^+), 248, 249 (70, 47, M^+-O), 220, 222 (95, 65, M^+-N_2), 185 (34), 150 (100), 84 (95). ^{1}H NMR, δ 7.71 - 7.96(5H,m), 8.63 – 8.66.(1H,d,d).

Anal. Found : C, 54.25; H, 2.13; N; 11.12; Cl, 26.90. Calcd for $C_{12}H_6N_2Cl_2O$: C, 54.19; H, 2.27; N; 10.53; Cl, 26.66.

2,2`-Dichloro-6,6`-diiodobiphenyl (2c). A solution of (2b) (13.58g, 53.67 mmol) in conc HCl (74 mL) and water (74 mL) was tetrazotised at 0°C by the slow addition of sodium nitrite (11.29 g) in water (30 mL). A conc. solution of KI (41.88g) in 5% aqueous H_2 SO_4 was then added slowly and the mixture was stirred for 1hr. The temperature was kept below 10°C. The solution was worked up and after recrystallisation of the crude product from ethanol, gave the diiodo-compound (2c) as white crystals (11.11g, 44%), mp 177-178°C.

^{1}H NMR, δ 7.5 (2H,dd, H-3/H-3`), 7.01 (2H,t, H-4/H-4`) and 7.87(2H, dd, H-5/H-5`), $J_{3,4}$ =8 Hz, $J_{3,5}$ = 1.22 Hz and $J_{4,5}$ = 8Hz. MS m/z 474(M$^+$). Anal. Found : C, 30.68; H, 1.42; Cl, 14.71; I,53.12. Calcd for C_{12} H_6 $C1_2$ I_2 : C,30,35; H, 1,27; C1, 14.93; I,53,44%.

1,8-Dichlorobiphenylene (5)

a) From 2,2`-dichloro-6,6`-diiodobiphenyl (2c). The diiodo-compound (2c) (1.73g, 3.78 mmol) was heated at 240°C (silicon-oil bath) while copper (2g) was added in small portions with manual stirring during 30min. The reaction mixture was worked up, similar to compound (2a). The crude product (0.94g) was chromatographed on alumina with ethyl acetate-light petroleum (1:3) as eluent and gave a mixture of (2c) and the required product (5). Separation was effected by sublimation under reduced (water-pump) pressure, giving 1,8-dichlorobiphenylene (5) (0.5g, 78%) as colorless crystalline solid, mp 128.5-129 °C.

^{1}H NMR,δ 6.70-6.72 (4H,m, H-2/H-7/H-3/H-6) and 6.53 (2H,dd, H-4/H-5), $J_{3,4}$=5.68Hz and $J_{4,2}$=2Hz. MS m/z 220(100, M$^+$), 150(39, M$^+$ -2Cl). Anal. Found : C, 65.04 ; H, 2.76 ; Cl, 31.99. Calcd for $C_{12}H_6Cl_2$: C, 65.19 ; H, 2.74 ; Cl, 32.07 %.

b) From 1,10-dichlorobenzo [c] cinnoline (3). The cinnoline (3) (3g, 12 mmol) was sublimed at 160°C/5x10^{-3}mm through a 50 cm silica furnace tube held at 800°C (reaction time ca.4hr) to give a greenish crystalline solid.

Crystallisation of the product from ethanol gave (in two crops) 1,8-dichlorobiphenylene (5) (2.25g, 84.5 %) as a yellow-green needles, mp 125-126 °C. Further purification by sublimation gave white crystals, mp 128,5-129 °C.

Preparation of the cyclo-octatetraene derivative (10a)

* All the equipments were dried, evacuated very well and flashed with nitrogen several times as well in order to get good conditions for the reaction.

A mixture of triphenylphosphine (Ph_3P), (0.4g, 1.52 mmol) nickel chloride ($NiCl_2$), (0.026g, 0.2 mmol), and zinc dust (0.4g, 6.12N mmol), was placed in a 50 ml round-bottomed, two necked flask, then the flask was evacuated and filled with nitrogen several times, then dry dimethylformamide 5ml was added. The flask was then placed in an oil bath at 50-80 °C, the contents being stirred magnetically for 3 hr, or until the complex catalyst had formed as a brownish solution, a nitrogen-purged solution of 1,8-dichlorobiphenylene (0.100 g, 0.46 mmol) in dry dimethylformamide 5 ml was flashed under nitrogen and added. The reaction mixture was stirred at 50–80 °C for 7 days, then cooled and filtered. The filtrate was diluted with water, and the precipitated product was filtered off, washed several times with water, and dried. This crude product was stirred at reflux with methyl iodide 12 ml for 30 min, and the mixture was cooled and filtered, the solvent was evaporated under reduced pressure, to give the crude product as a brown oil which was shown by TLC to be a mixture of six spots, then it was separated by crashing the alumina TLC plates, using ethyl acetate- hexane (1:3) as eluent, gave the cyclo-octateraene derivative (10a), yielding (40 mg, 30 %), after recrystallisation from ethanol, m.p.187–189 °C.

Mass spectrum m/z (%) 300 (23, M$^+$), 150 (60), 84 (100),

Anal. Found : C, 96.21 ; H, 4.15. Calcd for $C_{24}H_{12}$: C, 95.97 ; H, 4.03.
and trichloro-bis(biphenylenyl (10b) which was recrystallised from ethanol, yielding (60 mg, 68.93 %), m.p.195 – 196 °C. Mass spectrum m/z (%) 406, 408, 410 (M$^+$).

Nitration of 1,8-dichlorobiphenylene (5). Compound (5) (0.54g, 2.43mmol) and 1-nitro-pyrazole (1.35g, 1.195 mmol) were dissolved in CH_2Cl_2 (5 ml), and a solution of boron trifluoride etherate (1 mL) in CH_2Cl_2 (5 mL) was added. The reaction mixture was stirred at 25°C under dry nitrogen over night then quenched with ice-water and extracted with ether and washed with 5% aqueous sodium bicarbonate (25 mL) dried, and evaporated to give an oil which solidified on standing. The product was chromatographed on alumina, using toluene-hexane (1:3) as eluent. After a forerun of starting material (5) (0.15g), there was obtained 1,8-dichloro-3-nitrobiphenylene (11a) (0.26g, 40%) as deep yellow needles, mp 175-176°C after recrytallisation from ethanol.

^{1}H NMR, δ 7.33 δ (1H,d, H-2), 7.77 (1H,d, H-4), 6.54 (1H, dd, H-5), 6.89 (1H, t, H-6) and 6.72 (1H, dd, H-7), $j_{2,4}$=1.49Hz, $j_{5,6}$=7.48Hz and $j_{5,7}$=1.71Hz. MS m/z 265(100, M^+), 235(20), 219(50, M^+ - NO_2), 184 (91), 149(66). Anal. Found : C, 53.80; H,2.10; Cl, 26.64; N, 4.96. Calcd for $C_{12}H_5Cl_2NO_2$: C, 54.17; H, 1.89; Cl, 26.65; N, 5.26 %.
A third fraction from the chromatography column gave 1,8-dichloro-2-nitrobiphenylene (11b) (0.235g, 36%) as deep yellow needles, mp 166-167°C (from ethanol).

^{1}HNMR, δ7.5 (1H,d,H-3), 6.(1H,d,H-4), 6.71 (1H,t,H-5) and 6.88 (2H,d, H-6/H-7) (deceptively simple), $j_{3,4}$ = 7.48Hz, $j_{5,6}$ = 7.48 Hz and $j_{6,7}$ = 3,85 Hz. MS m/z 265(100,M^+), 235 (20), 219 (50, M^+-NO_2), 184(91), 149(66). Anal. Found : C, 54.26; H, 2.08; Cl, 26.42; N,5.37. Calcd for $C_{12}H_5Cl_2NO_2$: C, 54.17; H, 1.89; Cl, 26.65; N, 5.26%.

2,2'-diodo-4-nitobiphenyl(15) .the iodonium bisulfate(14). (71.3g,191.7 mmol).was stirred with soduim iodide (57.04g,380.3mmol) and copper(I) iodide(0.80g) in dry DMF (280ml)at reflux for 3hr .the solid was cooled to 70-80C°,water(150ml) was added dropwise with stirring ,and the mixture was allowed to stand for several hr until cold. The solid was filtered off, stirred with warm(ca 40 C°) water (400ml),filtered off ogain, dried, and finally recrystallized from ethanol to give 2,2'-diiodo-4- nitrobiphenyl as a dull yellow solid(54.0g, 63%), m.p.131-133C° . Found:31.86;H1.51;N,3.06;I,56.40.$C_{12}H_7I_2NO_2$ requires C31.98;H 1.55 ;N, 3.10;I, 56.27%. MS m/z 451(19M^+), 324(100, M^+-I),278(39), 150,151 ,(53,69, M^+-2I).

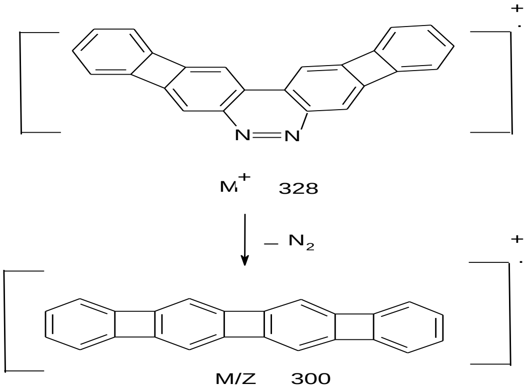
2- nitrobiphenylene (16). The diiodo –compound (15) (5.0g,11.1mmol) was heated at 235-240 C° (silicone oil bath) while copper bronze (4.0g) was added in small portions during 1hr ,with manual sttiring (copper wire) between each addition .The mixture was heated for a further 30min , then cooled and extracted with several portions of boiling acetone . the combined extracts were filtered, and the filtrate was evaporated under reduced pressure . the crude product was chromatographed on alumina with toluene –hexane (1:1) as aluent to give the nitro –compound_(0,67g,31%) ,m.p 105-107 C°).

2-amino-3-nitrobiphenylene(17).

A solution of 2-nitophenylene (16) (0,44g,2.23mml) and hydroxylamine hydrochloride (1.1g) in methanol(30ml) was stirred rapidly at 50-60 C°, and potassium hydroxide (2,2) was added in one portion.after 30 min at this temperature . the methanol was removed rapidly under reduced pressure , and the residue was washed with water.
After being dried , the product (0.41g) was dissolved in benzene and chromatophraphed on a n alumina colum . elution with benzene gave starting material (300mg) and then requires amino –derivative (17) (210mg, 45%), obtained as red needle ,m.p 220-221 C° (lit.[10] 219-221 C°). MS m/z 212(100,M^+) , 182(13) ,166(20) ,139(61).
Further elution gave the biphenylenopyridazine (18) (120mg15%) as yellow crystals .m.p 318-320 C°.
Found M^+,328,0986, $C_{24}H_{12}N_2$ requires M^+ 328,1004 MS m/z 328(100, M^+). 300(16, M^+-N_2).

RESULTS AND DISCUSSION

In an approach to (10a) using a direct coupling reaction it is evident that 1,8-dihalobiphenylenes (5) would be suitable starting material. The preparation of (5) as this material proved much easier to prepare in reasonable quantities, starting from commercially available 3-nitro-1,2-dichlorobenzene. A normal lothrop synthesis[3] was first investigated. 2,2`-Dichloro-6-6`-dinitrobiphenyl (2a) was prepared in good yield by Ullmann coupling reaction with copper bronze at 250°C. reduction of (2a) with tin (II) chloride dihydrate in hydrochloric acid or better, with Raney nickel and hydrazine hydrate in ethanol, gave 2,2`-diamino-6,6`-dichlorobiphenyl (2b) in high yields. However, some samples of Raney nickel gave mixtures of the diamine (2b) with 1,10-dichlorobenzo [c] cinnoline (3). Tetrazotisation of the diamine (2b) followed by treatment with aqueous potassium iodide gave the required 2,2`-dichloro-6,6`-diiodobiphenyl (2c) in good yield. Reaction of (2c) with copper bronze at 240°C,gave , after purification by vacuum sublimation and crystallisation, 1,8-dichlorobiphenylene (5) in 65% yield. The ^{1}H nmr spectrum showed an upfield shift for the aromatic protons in (5) compared with those in (2c) and can presumably be attributed to the paramagnetic ring current in the 4-membered ring[4]. Vacuum pyrolysis of (3) at 800°C, following McBride's method[5] for preparing biphenylene from benzo [c] cinnoline, gave almost pure (5) in high yields. Owing to the difficulty of separating (5) from the starting material (2c) in the Lothrop-type synthesis, the route via dichloro-benzo [c] cinnoline (3) was preferred. The cinnoline (3) was also obtained in 70% yield, by oxidation of (2b) with phenyl iodosodiacetate in dry benzene, similar to the method used by Barton and coworkers[6]., it was decided to attempt preparation of the hydrocarbon (10a) by using nickel-chloride and reducing metals,[7] the 1,8- dichlorobiphenylene (5) was treated with nickel-chloride, triphenylphosphine and zink dust in dry dimethylformamide. The reaction mixture was stirred and heated at 60 – 80 °C and followed by TLC during seven days, then allowed to attain at room temperature, column chromatography on silica gel of the product which was shown by TLC to be a mixture of several compounds, gave the expected cyclo-octatetraene derevative (10a), (30 %) The mass spectrum of the (10a) showed a parent ion at m/z 300 corresponding to the molecular ion of (10a), another fragment at 150 corresponding to dehydrobiphenylene species and another peak at m/z 84. The ^{1}H nmr spectra of (10a) contained a doublet at 5.66-5.85 ppm, for 4H, another multiplet at δ 5.90-6.16 ppm for 4H, and doublet at 5.85-5.87 ppm for 4H (J $_{1,2}$ = 5.5 Hz and J $_{2,3}$= 5.5 Hz), another hydrocarbon was isolated possibly, the trichlorobisphenylenyl (10b). The mass spectrum of (10b) showed a group of a parent ions at m/z 406, 408, and 410 corresponding to the molecular ion of (10b), the ^{1}H nmr of trichloride (10b) exhibited a complex multiplet at δ 7.28-7.33 ppm, and an inseparable crude mixture of unidentifiable compounds.



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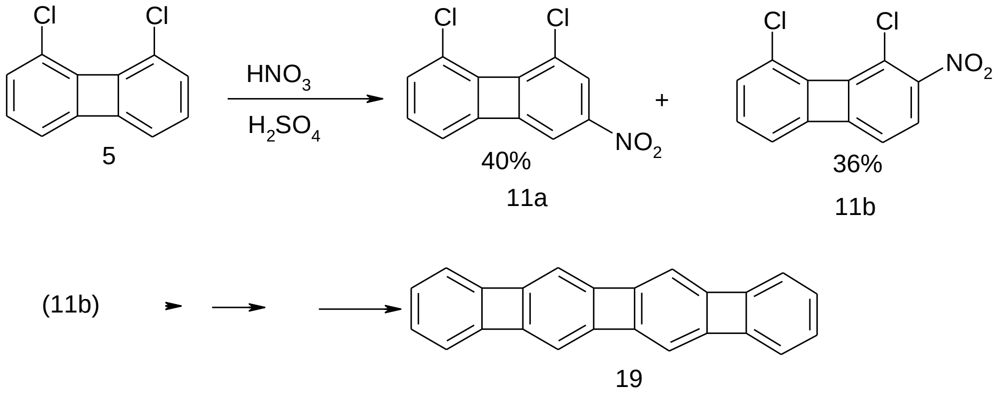
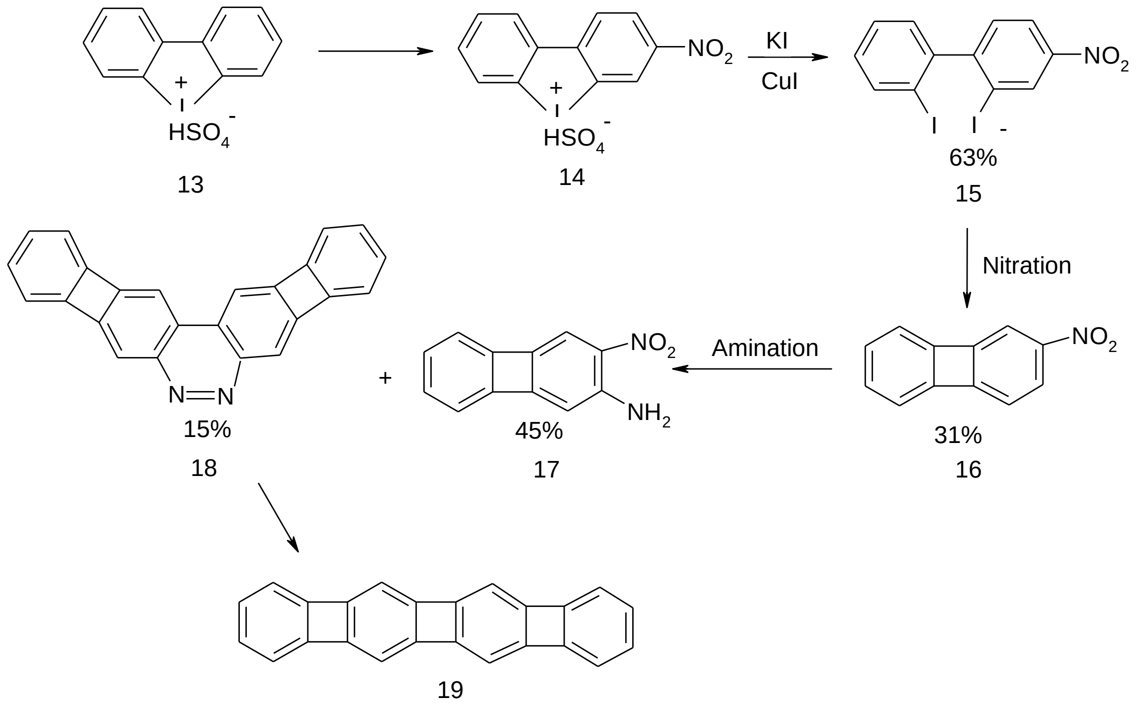
In order to activate one of the chlorine atoms, a nitro group was introduced at the ortho-position. The nitration procedure used was the one which gave good results with biphenylene itself. Nitration of (5) by using Olah and coworkers procedure[9] gave a mixture of products. Chromatography on alumina gave starting material together with 1,8-dichloro-3-nitro-biphenylene (11a), and its isomers 1,8-dichloro-2-nitro-biphenylene (11b). Elemental microanalysis for these two isomer (11a), (11b) were consistent with the molecular formula $C_{12}H_5Cl_2NO_2$. The ^{1}H nmr spectral data gave evidence for the positions of nitro-groups.



Scheme III

The 1,8-dichloro-2-nitrobiphenylene (11b) could be used as itermediate to prepare the very interesting compound such as [4]phenylene (19)m but the lack of time does not permit, the authors to investigate this route.

In connection of this work some strained molecules were prepared by using biphenylene iodonium sulphate as starting material, the nitrobiphenylene was obtained from the known iodonium salt(13) which was prepared by nitration of biphenylene-2,2'-iodonium hydrogen sulphate(13) with potassium nitrate. Compound (14) was converted into 2,2'-diiodo-4-nitrophenylene.(15).by reaction with sodium iodide and cuprous iodide refluxing dimethyl formamide. Heating(15) with copper bronze at 240 °C then gave (16) in 31% , then 2-amino-3-nitrobiphenylene(17) was prepared with hydroxylamine hydrochloride and potassium hydroxide according to Barton's method.[10] An unexpected but possibly useful by-product (18)



Scheme IV

In up to 10%, this type of reductive cyclisation to pyridazine derivative has been observed previously[11]. as shown overleaf. The biphenylenopyridazine structutre for compound(16). was supported by spectroscopic evidence .The mass spectrum showed a base peak at m/z 328 for parent ion of (18), and another peak corresponding to the loss of 28 mass units to give a species which was possibly (19) .The H nmr specetrum of (18) exehibited two singlets at 7.83 and 7.30 ppm for H_a and H_b respectively, these assigned by comparison with the spectrum of benzo[c]cinnoline,[12] and a multiplet at 6.99-7.09 ppm for protons c,d,e,and f.

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