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NICKELOCENE INTERACTION WITH *o*-HALOGENATED AZOBENZENES. 4-PHENYL-4H-CYCLOPENTA[*c*]CINNOLINE, A NEW PSEUDO-AZULENE

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SUMMARY

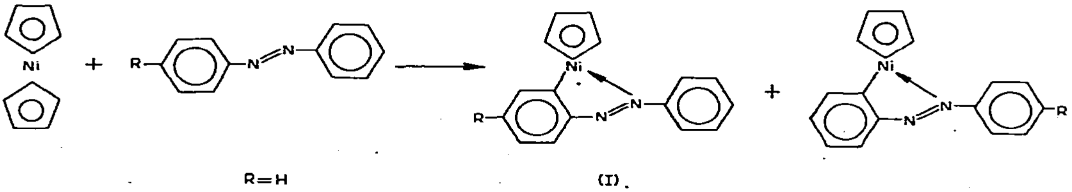
Nickelocene interacts with *o*-halogenated azobenzenes in two steps. Cyclopentadienyl[2-(phenylazo)phenyl]nickel(I) formed initially reacts with the *o*-halogenated azobenzene to give 4-phenyl-4H-cyclopenta[*c*]cinnoline(II).

o-Halogenated azobenzenes oxidize and dehydrate the complex(I) in this reaction. Compound(II) includes the "azobenzene fragment" of molecule(I). PMR spectra of (II) and its dimethylated analogue are interpreted.

INTRODUCTION

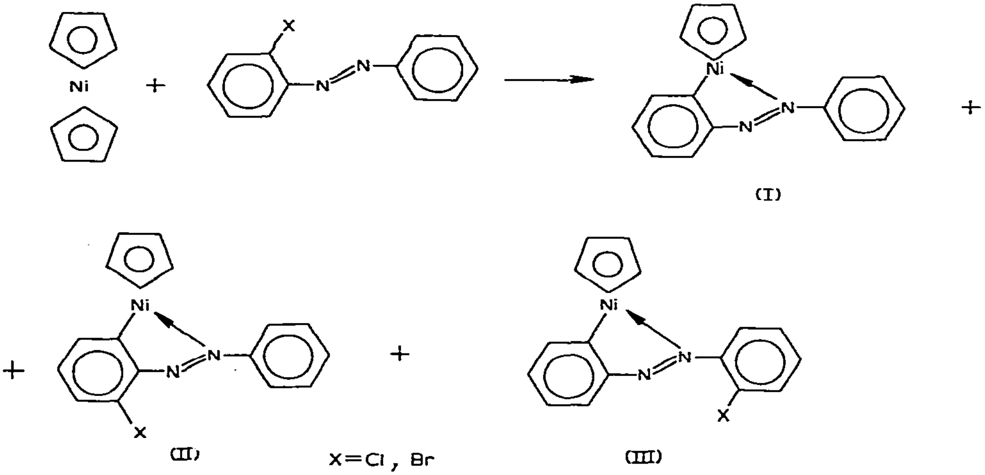
When studying the ligand exchange in nickelocene[1] we attempted a model reaction, the interaction of nickelocene with substituted azobenzenes[2]. Kleiman and Dubeck were the first to describe a reaction of nickelocene with the unsubstituted azobenzene[3]. They obtained cyclopentadienyl[2-(phenylazo)phenyl]nickel(I), the reactions and PMR spectra of which we have reported recently[2]. The azobenzene complexes of palladium, platinum, rhodium, iron etc. have been reported[4-7] (which contain a metal-to-carbon sigma-bond).

We have found that azobenzenes substituted in *para* position with groups like $(CH_3)_2N$, CH_3O, CH_3, F, Cl, $COOCH_3$, CN, or NO_2 react with nickelocene to give the complexes of type (I). Detailed syntheses and properties of the compounds will be published soon.



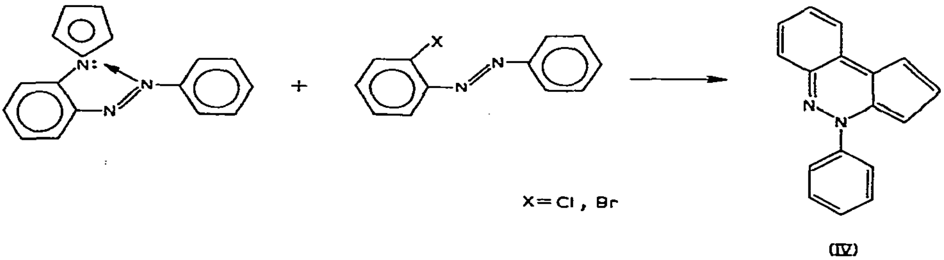
RESULTS AND DISCUSSION

In case of *o*-halogenated azobenzenes, nickelocene reacts abnormally. The halogen atom only is substituted and (I) alone is formed instead of a possible mixture of (I), (II), and (III). The complex, (I), is identical to the compound produced by the reaction of nickelocene with unsubstituted azobenzene. The rate of the formation of (I) increases in the series azobenzene, *o*-chloroazobenzene, *o*-bromoazobenzene.



Such an increase might be explained either by the fact that the halogen is initially coordinated by the nickelocene nickel whereby azobenzene would be orientated favourably with respect to nickelocene or that an electron is transferred from nickelocene to azobenzene whereby the ion pair is formed followed by elimination of the halogen and formation of the final product.

However, cyclopentadienyl[2-(phenylazo)phenyl]nickel formed from nickelocene and *o*-halogenated azobenzene undergoes further transformations. It reacts with the azobenzene to give a new non-benzenoid aromatic compound, a pseudo-azulene, 4-phenyl-4H-cyclopenta[*c*]cinnoline (IV)



Complex (I) disappears from the reaction mixture after 4.5 h with *o*-chloroazobenzene or ten minutes with *o*-bromoazobenzene. Earlier, we obtained compound(IV) from complex (I) by perbenzoic acid oxidation[2]. Its structure is established by UV and NMR data, mass spectra, elemental analysis, and chemical properties.

4-Phenyl-4H-cyclopenta[*c*]cinnoline is a crystalline compound dark-blue to almost black in colour, stable towards concentrated inorganic acids or alkalies in alcohol, soluble in most organic solvents giving intense blue solutions. Its UV spectrum is very close to that of azulene (Fig. 1). The molecular ion (*m/e* 244) is most

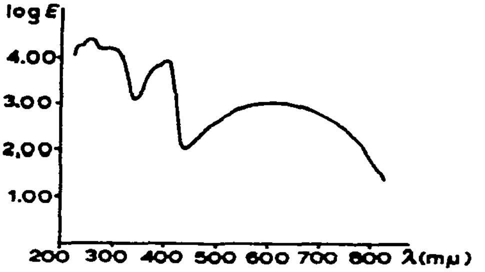


Fig. 1. UV spectrum of 4-phenyl-4H-cyclopenta[c]cinnoline in isooctane.

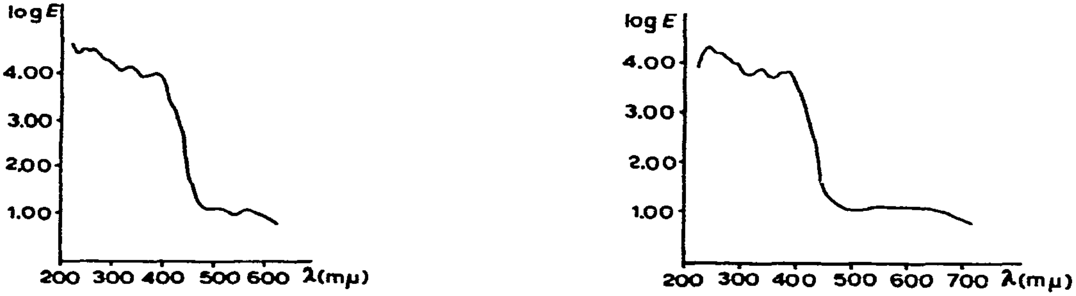


Fig. 2. UV spectrum of (IV) dissolved in (a) concentrated HCl or (b) 0.1 *N* HCl in CH_3OH.

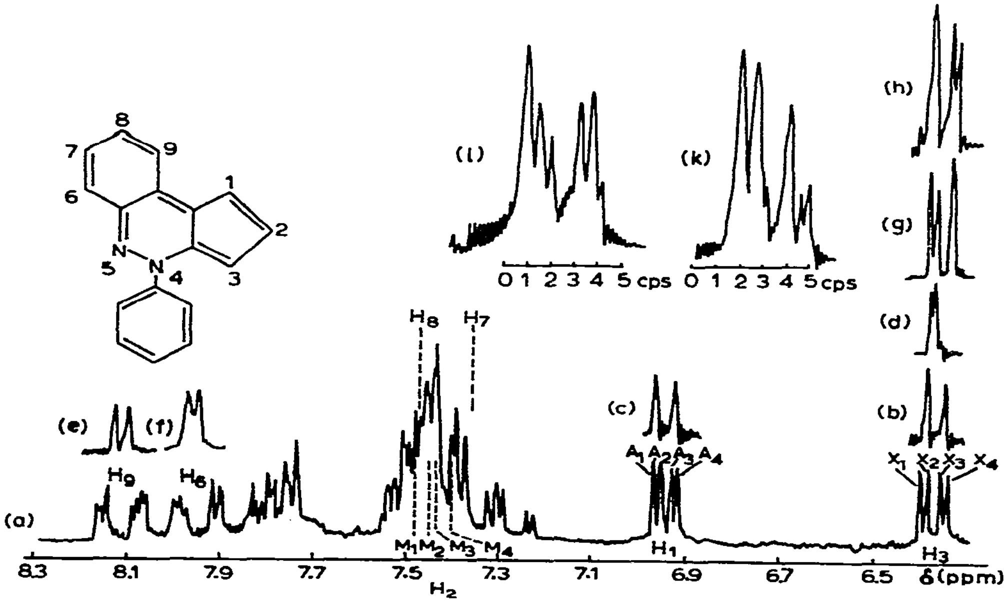


Fig. 3. PMR spectra of 4-phenyl-4H-cyclopenta[c]cinnoline in CS_2 solution (at 100 MHz): (a) normal spectrum; (b) H_3 signal at irradiation of H_1 (spin decoupling), abbreviated: H_3 at H_1 (s.d.); (c) H_1 at H_3 (s.d.); (d) H_3 at H_2 (s.d.); (e) H_9 at H_8 (s.d.); (f) H_6 at H_7 (s.d.); (g) H_3 at A_2A_4 doublet (tickling); (h) H_3 at A_1A_3 doublet (tickling); (k) H_3 at M_2 transition (selective irradiation); (l) H_3 at M_4 transition (selective irradiation).

pronounced in the mass spectrum, which indicates aromaticity of the compound. The molecular weights, found and calculated, coincide exactly. Basicity of (IV) is confirmed by its solubility in strong acids or by the variation in the UV spectrum (Fig. 2).

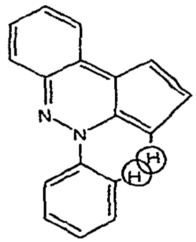
TABLE 1

CHEMICAL SHIFTS AND SPIN–SPIN COUPLING CONSTANTS IN THE SPECTRUM OF (IV)

Protons	δ(ppm)	J(Hz)	Protons	δ(ppm)	J(Hz)
H_1 (A)	6.960	1.3 (J_{AX})	H_6	7.969	2.1 (J_{68})
H_2 (M)	7.456	3.3 (J_{AM})	H_7	7.347	7.9 (J_{67})
H_3 (X)	6.396	4.4 (J_{MX})	H_8	7.478	7.6 (J_{89})
			H_9	8.130	3.2 (J_{79})

Compound (IV) resembles other azulenes in that it decomposes in glacial acetic acid[8,9] or at intermediate acidities, *e.g.* when its acid solutions are neutralized slowly.

The PMR spectrum taken in CS_2 solution (Fig. 3, Table 1) shows aromatic protons only. The doublet pairs, each pair corresponding to one proton (integral intensities), which have chemical shifts of 6.40 or 6.96 ppm are part of the AMX spectrum formed by protons of the five-membered rings. The high-field signal (at 6.40 ppm) should be assigned to proton H_3 because ring currents of the adjacent phenyl nucleus may significantly contribute here. Molecular models show that the nucleus somewhat declines from the molecular plane through space "overlap" of the hydrogens.



The signal at 6.96 ppm is assigned to proton H_1 while the doublet pair of proton H_2 is obscured by a multiplet centered at 7.44 ppm. Spin decoupling shows proton H_2 to have a chemical shift of 7.456 ppm. Selective irradiation, or tickling shows that the three spin–spin coupling constants coincide as to their signs. Parameters of the AMX spectrum are given in Table 2. A multiplet centered at 7.80 ppm (integral intensity 2) belongs to *ortho* protons of the phenyl ring while downfield signals at 8.130 or 7.969 ppm belong to protons H_9 or H_6, respectively, and chemical shifts of protons H_7 or H_8 found by double resonance are 7.347 or 7.478 ppm. This assignment follows from comparing the spectrum of (IV) with the spectrum of its dimethylated analogue, (V), *cf.* Fig. 4. The data above prove the structure of the compound obtained, (IV), unambiguously.

It is interesting to find out which "azobenzene fragment" enters the molecule (IV) when complex (I) reacts with *o*-chloroazobenzene, the fragment already present in the molecule (I) or that belonging to *o*-chloroazobenzene.

TABLE 2

FREQUENCIES IN THE AMX SPECTRUM

Frequency (Hz)	Frequency (Hz)	Frequency (Hz)
A_1 698.3	M_1 749.5	X_1 624.2
A_2 695.0	M_2 746.2	X_2 641.1
A_3 697.0	M_3 745.1	X_3 638.1
A_4 693.7	M_4 741.8	X_4 636.6

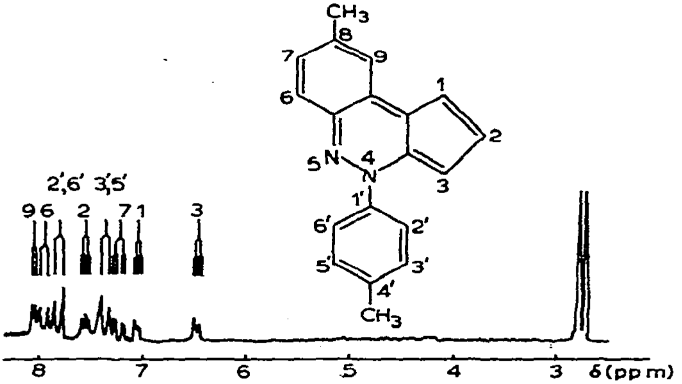
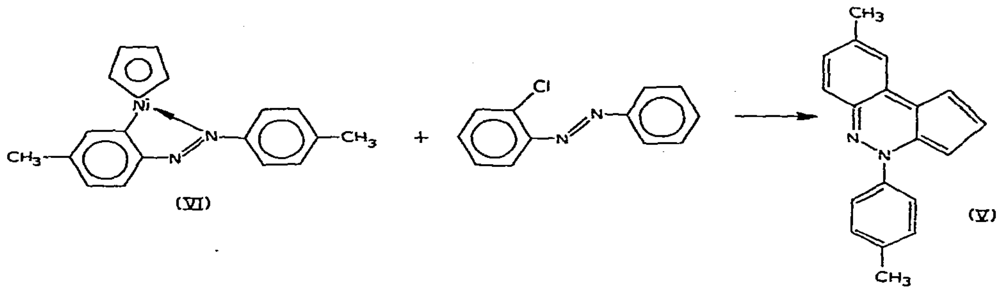


Fig. 4. 4-*p*-Tolyl-8-methyl-4H-cyclopenta[*c*]cinnoline dissolved in CCl_4. PMR spectrum at 100 MHz.

An analogue of (I) containing two methyl groups at positions 3 and 8, (VI), reacts with *o*-chloroazobenzene to produce 4-*p*-tolyl-8-methyl-4H-cyclopenta[*c*]-cinnoline only, thus the "azobenzene fragment" of (V) appears there from (VI).



The structure of (V) is verified by its PMR spectrum which readily allows the first-order interpretation, Fig. 4. Hence, *o*-chloroazobenzene may act as a mild dehydrating agent here.

We are studying electrophilic substitutions in compound (IV). The results, as well as the Hückel MO calculation of the compound, will be published soon.

EXPERIMENTAL

Nickelocene was obtained according to the method of Cordes[10]. *o*-Chloro- or *o*-bromoazobenzenes were obtained from the respective *o*-halogenated nitrosobenzenes condensed with aniline in glacial acetic acid. *p*-Azotoluene was obtained by condensing *p*-methylnitrosobenzene with *p*-toluidine. These were purified by chromatography on alumina.

Cyclopentadienyl[2-(phenylazo)phenyl]nickel from nickelocene and o-chloroazobenzene

Absolute *o*-xylene (16 ml) was distilled in an argon atmosphere to a mixture of nickelocene (0.31 g, 1.64 mmole) and *o*-chloroazobenzene (1.42 g, 6.6 mmole) and the resulting mixture was stirred and refluxed in an argon atmosphere for ten minutes. The mixture was cooled, diluted with an equal volume of hexane, and chromatographed on alumina (activity III to IV). A dark-violet band was eluted by hexane/benzene (1/1). Repeated chromatography gave 0.22 g (47%) of cyclopentadienyl-[2-(phenylazo)phenyl]nickel whose IR and NMR spectra were identical to those of the sample obtained from azobenzene and nickelocene.

4-Phenyl-4H-cyclopenta[c]cinnoline

From nickelocene and o-chloroazobenzene. The reaction differs from the preceding one only in that the mixture was refluxed for 4.5 h. The mixture was cooled, diluted with two volumes of hexane, and chromatographed on alumina. A dark-blue band* was eluted by benzene/hexane (1/2). After removal of the solvent 0.13 g (32.1%) of 4-phenyl-4H-cyclopenta[*c*]cinnoline were obtained, m.p. 121°**. (Found: C, 83.34; H, 4.98; N, 11.46. $C_{17}H_{12}N_2$ calcd.: C, 83.59; H, 4.95; N, 11.47%.)

From nickelocene and o-bromoazobenzene. The reaction differs from the preceding one only in that the mixture was refluxed for ten minutes. 0.09 g (22%) of 4-phenyl-4H-cyclopenta[*c*]cinnoline was obtained.

Cyclopentadienyl[2-(4-tolylazo)-5-methylphenyl]nickel

Absolute *o*-xylene (16 ml) was distilled in an argon atmosphere to a mixture of nickelocene (0.31 g, 1.64 mmole) and *p*-azotoluene (1.39 g, 6.6 mmole), and the resulting mixture was stirred and refluxed for 15 h. The mixture was cooled, diluted with an equal volume of hexane, and chromatographed on alumina. A violet band was eluted by benzene/hexane (1/1). Repeated chromatography gave 0.18 g (33%) of cyclopentadienyl[2-(4-tolylazo)-5-methylphenyl]nickel, m.p. 112–113°. (Found: C, 68.62; H, 5.50. $C_{19}H_{18}N_2Ni$ calcd.: C, 68.52; H, 5.45%.)

4-p-Tolyl-8-methyl-4H-cyclopenta[c]cinnoline

Cyclopentadienyl[2-(4-tolylazo)-5-methylphenyl]nickel (1 g, 3 mmole) and *o*-chloroazobenzene (1.95 g, 9 mmole) dissolved in 35 ml of absolute *o*-xylene were refluxed and stirred in an argon atmosphere for 7.5 h. The mixture was cooled, diluted with an equal volume of hexane, and chromatographed on alumina. A blue

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* Unidentified compounds were present between the band of *o*-chloroazobenzene and that of 4-phenyl-4H-cyclopenta[*c*]cinnoline.

** Melting points are not corrected.

band was eluted by benzene/hexane (1/1). Repeated chromatography gave 0.38 g (40%) of 4-*p*-tolyl-8-methyl-4H-cyclopenta[*c*]cinnoline, m.p. 145°. (Found: C, 84.09; H, 5.99; N, 10.23. $C_{19}H_{16}N_2$ calcd.: C, 83.79; H, 5.92; N, 10.29%.)

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