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Electrosynthesis of Unsymmetrical Donor-Acceptor Polyaryls

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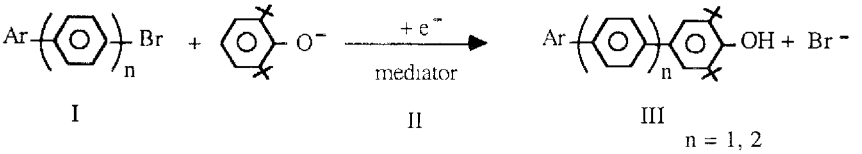
Abstract *Unsymmetrical Donor-Acceptor Polyaryls are synthesized by an electrochemically induced $S_{RN}1$ reaction using 2,6-ditertbutyl phenoxide as nucleophile and acceptor substituted polyarylbromides The latter are synthesized by a cross coupling reaction of aromatic organometallic reagents and aromatic halides catalyzed by palladium complexes*

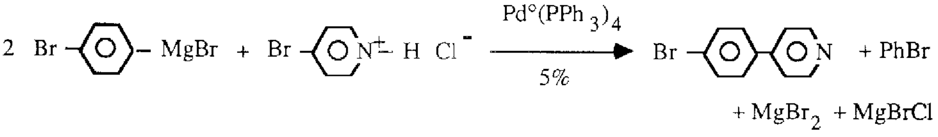
The hyperpolarizability properties of unsymmetrical donor-acceptor polyaryls D-$(Ar)_n$-A depend on the number (n) of aromatic rings present between the electron donating group D and the electron attracting group A It has been shown from theoretical calculations that the hyperpolarizability per unit volume of unsymmetrical polyaryls (A = NO_2, D = NMe_2) was maximum when n = 3 [1] It has been found by EFISH measurement (Electric Field Induced Second Harmonic Generation) that the hyperpolarizability β of unsymmetrical polyparaphenylenes (A = CN, D = NMe_2)[2] was maximum for quaterphenyls derivatives [3-5] In order to examine the dependance of the hyperpolarizability properties as a function of the number n of aromatic rings, we have synthesized a series of unsymmetrical polyaryls in which an hydroxy group is the donor group and the acceptor group is either a cyano group or a pyridyl ring [6] When the acceptor is a pyridyl ring, the resulting polyaryl should easily be transformed by alkylation and deprotonation to a zwitterion which could lead to interesting materials for non linear optics (liquid cristals, polymers) [7] Homologous donor-acceptor biaryls have been previously synthesized via an electrochemically induced $S_{RN}1$ reaction of phenoxide nucleophile with acceptor substituted arylbromides, in liquid ammonia [8,9] The same procedure was used to synthesize unsymmetrical donor-acceptor ter and quateraryls derivatives starting from polyarylbromides



(1)

Syntheses of the precursors I

p-Br-$(C_6H_4)_n$-CN (n = 1 (Ia), 2 (Ib)) were synthesized according to a previous procedure, a palladium catalyzed cross-coupling reaction between an organometallic reagent substituted by the donor group and an arylbromide substituted by the acceptor group[2]. Same method provided the p-Br-C_6H_4-4-pyridyl Ic.



(2)

To a mixture of 17 mmol of p-Br-C_6H_4-MgBr and 15 mmol of bromo-4-pyridine hydrochloride were added 0.75 mmol of Pd°$(PPh_3)_4$ and 18 mmol of p-Br-C_6H_4-MgBr. After reaction (12hrs) the mixture was treated with water and extracted with dichloromethane. Compound Ic was precipitated as the hydrochloride salt by acetone containing HCl. It was then dissolved in water. Addition of KOH 0.2 M made compound Ic precipitate (isolated yield 60%). This one step reaction is a new method presenting the advantage to use commercial starting materials by comparison to a reported synthesis[10].

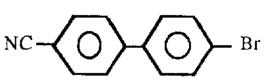
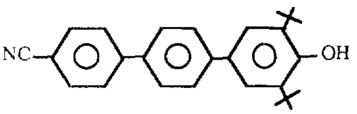
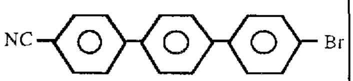
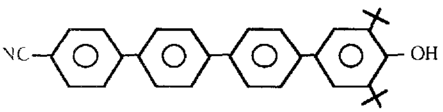
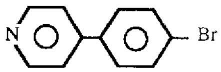
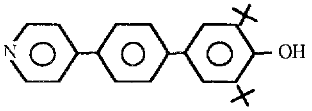
Electrosyntheses of donor-acceptor substituted polyaryls III

Donor-acceptor polyaryls (III) were synthesized from the polyarylbromides precursors I via an electrochemically induced $S_{RN}1$ reaction in the presence of a mediator (II) (reaction 1). Results are given in Table 1. The role of the mediator was to limit a competitive reaction: reduction of I[11,12]. The key reducing species of the process was then the reduced form of the mediator $II^{\circ -}$. 4,4'-bipyridine, quinoxaline or phthalonitrile were used as mediators. In the case of compounds IIIa and IIIb, yields were found to be independent of the mediator (4,4'-bipyridine or quinoxaline).

The 2,6-diterbutylphenoxide nucleophile was synthesized in situ by deprotonation of the corresponding phenol by potassium terbutoxide. The reaction was carried out in the presence of KOH to impede the protonation of $II^{\circ -}$[9]. Liquid ammonia is considered to be the best solvent for these electrochemically induced $S_{RN}1$ reactions[13] but in this case, due to the low solubility of compounds I in this solvent, tetrahydrofuran was used as a cosolvent. It is known that the yield of these reactions is not affected for volumic percents of cosolvent less than 20%[14]. Despite the presence of this cosolvent, compounds I were little soluble.

The electrosyntheses were carried out in an undivided electrochemical cell containing 80 mL of liquid ammonia at -40°C. 17 mmol of 2,6-diterbutylphenol, 2 mmol of water, 19 mmol of potassium terbutoxide and 1.5 mmol of the mediator II were successively introduced into the cell. 2 mmol of the polyarylbromide I dissolved in 20 mL of tetrahydrofuran were then added. A constant current density of 0.15 A/dm^2 was imposed between a platinum grid (1024 mesh, 0.09 dm^2) as the cathode and a magnesium rod as the anode.

Table 1 Results of the Electrosyntheses

Starting product I	Mediator II	Product III	Yield[(a)]
 Ia	4,4-bipyridyl or quinoxaline	 IIIa	25%
 Ib		 IIIb	<10%
 Ic	phthalonitrile	 IIIc	35%

(a) isolated product yield relative to I

The electrolyses were interrupted before total conversion of compounds I (about 50% for Ia and Ic, only about 20% in the case of Ib) in order to avoid possible secondary reactions, such as the attack of the cyano group by the bases. After neutralization of the solution by 20 mmol of ammonium bromide, ammonia was evaporated and the products were extracted with dichloromethane. IIIa and IIIb were purified by two successive flash chromatographies. The first one on silica gel with dichloromethane as eluent and the second one on a reverse phase Lichroprep RP 18 (230-400 mesh) with acetonitrile as eluent. IIIa and IIIb were recrystallized in acetonitrile. IIIc was purified by flash chromatography (silica gel and ethylacetate as eluent) and recrystallized in acetone. The products characterizations are given in note 15. Since the values β of products III are not yet determined, no effort have been developed for optimization [11] of electrosyntheses at this level of study. The isolated yields (relative to compounds I) were lower than 35 % due to low conversion rates, a consequence of the low solubility of the starting material I (mainly Ib) in liquid ammonia. Some difficulties in the purification of the unsymmetrical polyaryls were encountered due to their low solubility in most organic solvents. For the same reasons, no attempts have been made to synthesize molecules with larger number of phenyl units.

Conclusion

Non reported unsymmetrical donor-acceptor ter and quateraryls have been synthesized by an electrochemically induced $S_{RN}1$ reaction, performed in a mixture of liquid ammonia and tetrahydrofuran, starting from polyarylbromides synthesized by a palladium catalyzed cross-coupling reaction The main difficulty of these electrosyntheses was due to the low solubility of the starting polyarylbromides but nevertheless, this reaction provided acceptable chemical yields The non linear optics properties of products III are currently under investigation and will be reported later

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15 Products analysis

Ic,HCl ^{1}H NMR (250 MHz $CDCl_3$) δ ppm 2 45 (s 1H), 7 60 (d 2H J=7Hz), 7 73 (d 2H J=7Hz), 7 93 (d 2H J=5Hz), 8 78 (d 2H J=5Hz) MS m/z 236, 234 (M)

Ic m p 130°C ^{1}H NMR (250 MHz $CDCl_3$) δ ppm 7 50 (m 2H), 7 52 (d 2H J=8 7Hz), 7 64 (d 2H J=8 7Hz), 8 49 (m 2H) MS m/z 235, 233 (M) Anal Calcd for $C_{11}H_8BrN$ C, 56 43, H, 3 44, N, 5 98, Found C, 56 0, H, 3 50, N, 5 80

IIIa· m p 212°C ^{1}H NMR (250 MHz $CDCl_3$) δ ppm 1 51 (s 18H), 5 33 (s 1H(OH)), 7 45 (s 2H), 7 66 (s 4H), 7 74 (s 4H) ^{13}C NMR (63 MHz $CDCl_3$) δ ppm 30 31, 34 50, 110 67, 119 04, 123 97, 127 47, 127 59, 131 46, 132 63, 136 37, 136 98 142 62, 145 35, 153 91 MS m/z 384, 383 (M), 368, 179

IIIb m p 256°C ^{1}H NMR (250 MHz $CDCl_3$) δ ppm 1 51 (s 18H), 5 31 (s 1H(OH)), 7 46 (s 2H), 7 63-7 78 (m 8H), 7 75 (s 4H) ^{13}C NMR (63 MHz $CDCl_3$) δ ppm 30 34, 34 50, 110 87, 118 98, 123 95, 127 28, 127 46, 127 54, 127 61, 127 63, 131 83, 132 66, 136 30, 137 80, 138 08, 141 24, 141 70, 145 18, 153 72 MS m/z 460, 459 (M), 444, 84 Anal Calcd for $C_{33}H_{33}NO$ C, 86 23, H, 7 24, N, 3 05, Found C, 85 47, H, 7 28, N, 2 85

IIIc m p 231-233°C ^{1}H NMR (250 MHz $CDCl_3$) δ ppm 1 53 (s 18H), 7 47 (s 2H), 7 60 (d 2H J=6Hz), 7 68 (d 2H J=7 5Hz), 7 74 (d 2H J=7 5Hz), 8 69 (m 2H) ^{13}C NMR (63 MHz $CDCl_3$) δ ppm 30 27, 34 45, 122 34, 123 92, 127 21, 127 57, 132 34, 135 17, 136 39, 143 29, 148 42, 149 72, 153 94 MS m/z 359 (M), 344, 231 Anal Calcd for $C_{25}H_{29}NO$ C, 83 52, H, 8 13, N, 3 89, Found C, 83 60, H, 8 00, N, 3 75

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