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NITROCYCLOHEXADIENONES : A NEW CLASS OF NITRATING AGENTS

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Résumé : Nous utilisons des nitrocyclohexadiènones comme réactifs de nitration. Ces produits sont aisément accessibles à partir des perhalogénophénols correspondants ; ils sont stables et faciles à manipuler. L'élan moteur de la réaction est la réaromatisation du cycle du réactif qui conduit à la nitration dans des conditions particulièrement douces. Ces réactifs permettent la nitration directe et avec de bons rendements de composés très activés comme les dihydroxynaphtalènes.

Abstract : Various nitrocyclohexadienones are proposed as new nitrating agents. These compounds are easy to prepare from corresponding phenols, easy to handle and stable. Nitrocyclohexadienones act as nitronium carriers using rearomatization as the driving force and permit nitration of highly activated substrates under mild conditions and with good yields.

Nitration is one of the oldest known reactions and nitro-compounds are some of the more important building blocks used in organic synthesis. Despite widespread interest in this area of research, no general method for selective nitration of organic substrates has yet been devised. This is mainly because the classical nitrating species NO_2^+ is highly reactive (i.e. exhibits low selectivity) and has the ability to react as an oxidizing agent.

More light has been shed by chemo-physical studies (1) on the mechanism underlying this type of electrophilic reaction and new reagents and methods allowing nitration of specific substrates have been described in recent publications (2, 3). The only general methodology for nitration of highly activated aromatic substrates (aromatic ring with electron releasing substituents) involves the use of appropriate protective groups. Indeed this strategy has been used in many syntheses. The necessity for two supplementary steps (blocking and deblocking reactions) makes this process both costly and time consuming. Consequently the development of new selective reagents is still of high economic and scientific interest.

Abundant examples of highly reactive entity transfer with good selectivity exist in biological systems and in organic chemistry. Hydride transfer from dihydropyridine of NADH or structurally related systems is probably the most famous example (4a). Various halogenations have been performed using this process and in fact, CALO et al. were the first to suggest that direct bromination of anilines or phenols could be achieved using perbromocyclohexadienones (5).

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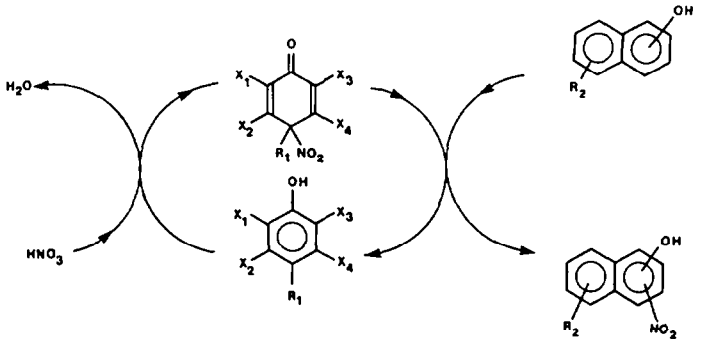
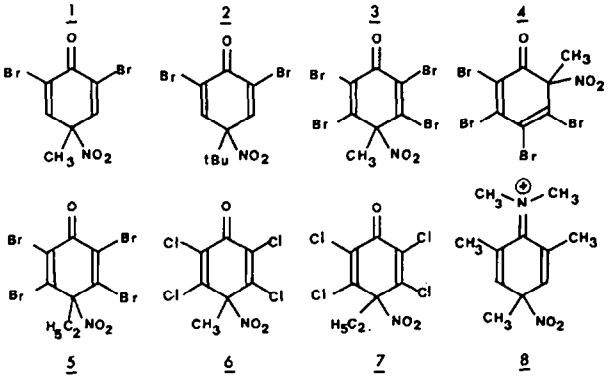
A certain number of reagents able to release reactive species during the course of an aromatization reaction (which is the key to selectivity control (4a)), have been designed in our laboratory over the last few years. We have previously described chemo and regioselective chlorination of various substrates using hexachlorocyclohexadienones (4b). All these examples illustrate that highly reactive species can be produced in mild conditions using aromatization as the driving force. Here we report application of this concept to selective nitration of sensitive substrates. Nitrocyclohexadienones are able to liberate nitronium species by aromatization. The free nitronium species can then react with substrate present in solution (scheme 1) (4c).



SCHEME 1 : Nitration using ring aromatization as the driving force : general scheme

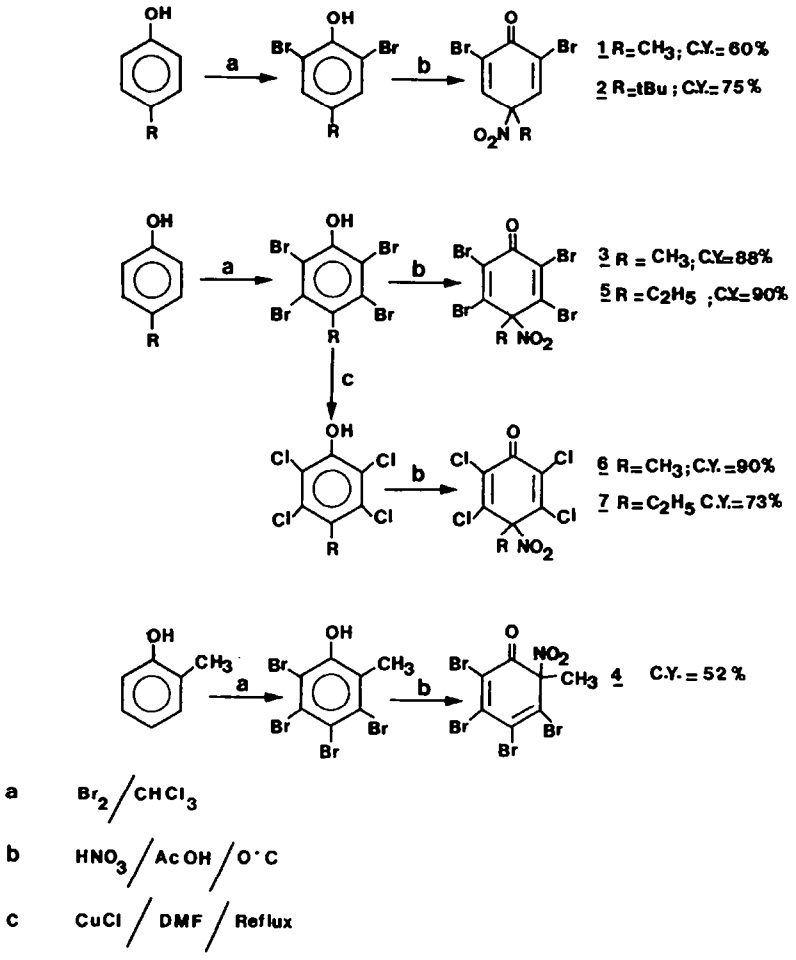
REAGENTS SYNTHESIS

Nitrocyclohexadienones described in the literature have generally been produced by ipso attack of substituted alkyl phenols using nitric acid. In this paper, we describe the synthesis of certain nitrocyclohexadienones (scheme 2) using a modification of the ZINCKE method (6). The nitrating properties of these products were also tested.



SCHEME 2 : Synthesized and tested nitrocyclohexadienones

Compounds 1 to 7 were readily prepared from corresponding phenols. Bromide intermediates were produced by reacting bromine with phenols in chloroform. Intermediate chlorophenols were produced by reacting cuprous chloride with bromo analogs (scheme 3). Compound 8 was obtained using the method described by RIDD and HELSBY (7).



SCHEME 3 : Synthesis of nitrocyclohexadienones 1 to 7

All reagents are crystalline compounds and easy to handle. The nitro compounds 1, 2, 3, 5, 6 and 7 are stable at room temperature. Product 4 has to be stored at 4°C however and 8 is particularly sensitive to moisture.

DETERMINATION OF REACTION CONDITIONS AND REAGENT TESTING

We have used 1-naphthol as the test substrate. This compound is highly sensitive. Reaction with nitric acid gave a number of nitro derivatives and a mixture of various oxidation products (table 1).

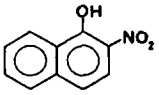
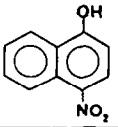
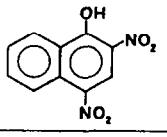
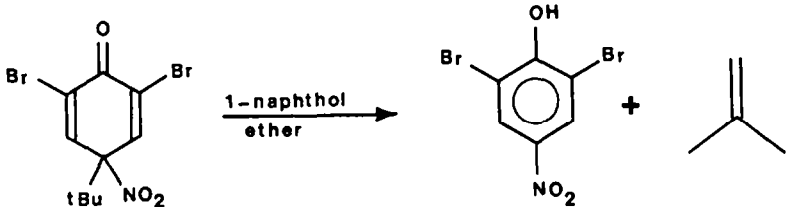
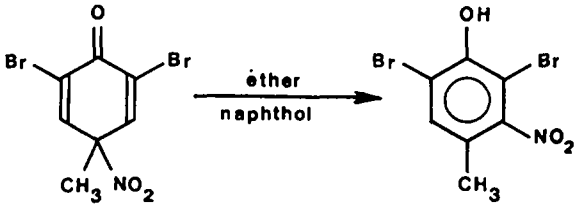
nitrating agents / product yields	HNO_3d = 1,52 CH_3COOH P_2O_5	HNO_3d = 1,52 CH_3COOH	HNO_3d = 1,49 CH_3COOH
	5,2 %	8,4 %	7,1 %
	0 %	0 %	0 %
	2,2 %	4,2 %	5,8 %
Oxidation products	92 %	87 %	87 %

TABLE 1 : Nitration of naphthol using nitric acid

No nitronium species were obtained in the case of 2,6-dibromo-4-nitro-4-tbutyl-2,5-cyclohexadien-1-one 2 because the t-butyl group is a better leaving group than the nitro group (scheme 4). Intramolecular rearrangement occurred in the case of 2,6-dibromo-4-methyl-4-nitro-2,5-cyclohexadien-1-one 1 (scheme 5).



SCHEME 4 : Ring aromatization of 2,6-dibromo 4-nitro-4-tbutyl-2,5-cyclohexadien-1-one 2



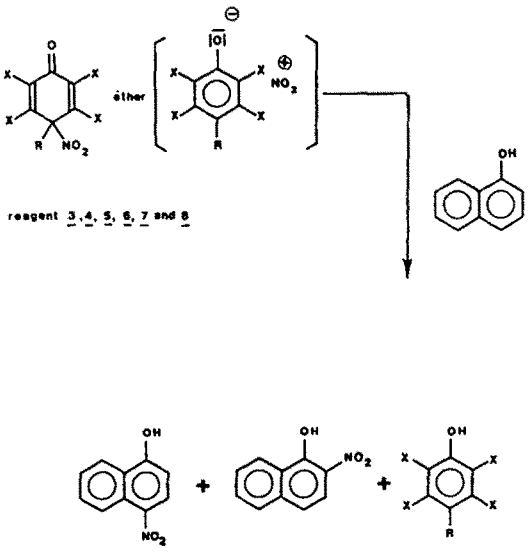
SCHEME 5 : Rearrangement of 2,6-dibromo-4-nitro-4-methyl-2,5-cyclohexadien-1-one 1

In contrast, reaction of nitro perbromocyclohexadienone 3 with 1-naphthol in various solvents gave mononitrated naphthols. Solvent or temperature effects (table 2) exerted little influence on

the 2-nitration to 4-nitration ratio of 1-naphthol (scheme 6). Dry diethyl ether which gives few oxidation products was chosen as solvent. Mononitration yields and ortho/para ratios using nitrocyclohexadienones with different geometry (reagent 4) and steric strength (reagents 5, 6, 7) or charged reagent 8, were nearly identical. This was ascribable to a loose ion pair mechanism (nitronium/phenoxy). The ion pair was formed during mutual approach of the reactants. Formation of this nitrating species probably occurs at the beginning of substrate/reagent approach without specific recognition of the reactants by non-covalent interactions (scheme 6). Such type of recognition has been observed with hexachlorocyclohexadienones (4a) and was recently proposed as the mechanism for the nitration of phenol using a pyridinium salt (8).

Entry	Solvent	Temp. °C	$\frac{\text{orthonitration}}{\text{paranitration}}$ ratio
1	diethylether	20°C	0,78
2	"	- 20°C	0,78
3	diisopropylether	20°C	0,75
4	tetrahydrofuran	"	0,82
5	chloroform	"	1,5
6	hexane	"	0,75
7	carbon tetrachloride	"	1

TABLE 2 : Solvent effect during nitration of 1-naphthol by reagent 3



SCHEME 6 : 1-naphthol nitration using nitrocyclohexadienones

Nitrocyclohexadienones act as nitronium carriers and permit nitration in mild conditions and in non-acidic solvents. The proposed reagents are attractive for nitration of 1-naphthol due to their high chemoselectivity rather than regioselectivity : mononitration yields rose to 66 % using this substrate (table 3, entry 1) whereas yields using nitric acid as reagent, were negligible. Formation of a reasonable amount of 4-nitro 1-naphthol is of special interest : the only described

method for the direct nitration of naphthol gives 2-nitro 1-naphtol and employs acetylnitrate as reagent which is known to be dangerous and difficult to handle (9). The perhalogenophenol by-products of the reaction were easily separated by chromatography or simple crystallization (see experimental part). The readiness of work-up can be further improved owing to the large number of available cyclohexadienones (scheme 2, R = CH_3, C_2H_5 ; X = Br, Cl, etc...). The possibility of recycling perhaloalkylphenols for the preparation of nitrocyclohexadienone reagents with high yield (90 %) makes this reaction even more attractive from an economical point of view.

NITRATION OF NAPHTHOLS AND NAPHTHOL-DERIVATIVES USING NITROCYCLOHEXADIENONES

We have used reagents 3 and 5 to prepare nitro products of substrates activated by electron releasing substituents (table 3).

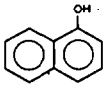
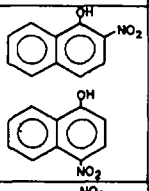
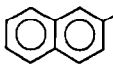
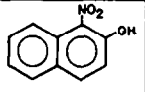
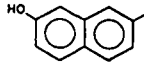
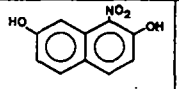
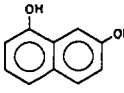
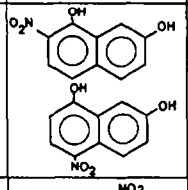
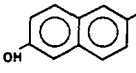
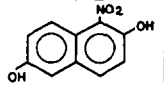
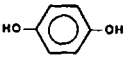
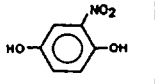
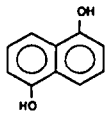
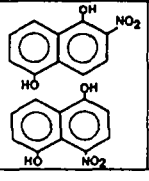
Entry	Substrates	Products	HNO_3 mononitrated yields	HNO_3 products ratios	Reagent 3 mononitrated yields	Reagent 3 products ratios	Reagent 5 mononitrated yields	Reagent 5 products ratios
1			1,3 %	majority -	66 %	43 % 57 %	67 %	45 % 55 %
2			21 %	-	56 %		53 %	
3			2,6 %	-	50 %			
4			8,2 %	majority traces	53 %	62 % 38 %	52 %	60 % 40 %
5			6 %	-	63 %		61,3 %	
6			0 %	*1 0 %	33,5 %	100 %	-	
7			0 %		49 %	49 % 51 %	48 %	50 % 50 %

TABLE 3 : Nitration of various phenols and naphthols by reagent 3 or 5

*1 benzoquinone was obtained with a 46 % yield

Table 3 shows that these particular nitro products cannot be synthesized by direct classical nitration using nitric acid. Nitrocyclohexadienones 3 and 5 in contrast gave high yields of mononitro products with all the substrates tested including the very sensitive dihydroxy aromatic compounds. The latter are known to give oxidation products easily and quinones were the main products obtained when nitric acid was used as reagent (see below, table 3).

Nitro-products of substrates activated by hydroxy, methoxy and/or acetoxy substituents were prepared using reagents 3 and 5. No regio-selectivity occurred in the case of 1-naphthol nitration (2-position/4-position nitration ratio = 1 ; entry 1, 4, 7 ; table 3).

In contrast the 2-naphthol gave chemospecific and regiospecific nitration at the 1-position with reagents 3 and 5 (entries 2,3,5, table 3) and in the case of naphthalenic substrates activated by hydroxy groups at both positions 1 and 2, the ring substituted at position 1 was specifically nitrated : no traces of 1-nitro 2-hydroxy product were observed in this case (entry 4, table 3).

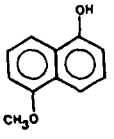
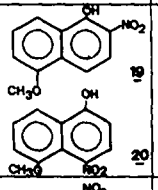
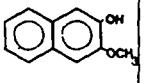
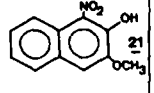
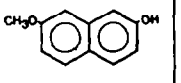
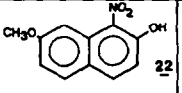
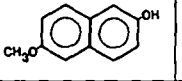
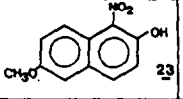
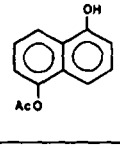
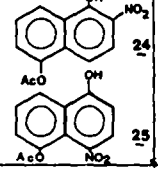
Entry	Substrates	Products	HNO_3		Reagent 3	
			mononitrated yields	products ratios	mononitrated yields	products ratios
1			1,3 %	majority -	66 %	55 % 45 %
2			11 %	*2 -	42 %	
3			2 %	*3 -	50 %	
4			< 1 %	*4 -	45 %	
5			< 1 %	majority -	72 %	52 % 42 %

TABLE 4 : Nitration of hydroxy, methoxy or hydroxy-acetoxynaphthalene by reagent 3

*2 3-methoxy-1,2-naphthoquinone was obtained with a 35 % yield

*3 7-methoxy-1,2-naphthoquinone was obtained with a 30 % yield

*4 6-methoxy-1,2-naphthoquinone was obtained with a 32 % yield

When the aromatic rings were activated by different electron releasing substituents or acetoxy groups, only the ring substituted by the hydroxy group was selectively nitrated. No nitration of the ring carrying the methoxy or acetoxy group was detected (table 4). It is interesting to note that while nitrocyclohexadienones gave selective mononitration with these different substrates, quinones (oxidation products) were the main products obtained using nitric acid.

CONCLUSION

Our study shows the potential of using the aromatization of cyclohexadienic reagents as the driving force for selective electrophilic substitution. Nitrocyclohexadienones act as carriers for nitronium species and permit selective and direct nitration of various substrates which are very sensitive to oxidation. Nitration of this type of compounds cannot be obtained with classical nitrating agents and up until now, nitro products could only be produced by indirect means. Both the simplicity of synthesis and stability of our new ready to use reagents plus the fact that the major by-product can be recycled, make the development of this type of nitrating agent particularly attractive.

EXPERIMENTAL

Diethylether was dried over Na. All other reagents and solvents were used as obtained from the supplier. ^{1}H-NMR spectra were obtained on a Perkin Elmer R 32 spectrometer (90 MHz) using deuterochloroform as solvent and tetramethylsilane as the internal standard. The positions of the signals are reported in units in ppm. The splittings of the signals are described as singlets (s), doublets (d), triplets (t), quartets (q) or multiplets (m).

IR spectra were recorded on a Perkin Elmer type 457 spectrometer using KBr discs for solids or neat films between NaCl discs ; the positions of the signals are described in cm^{-1}.

Reagent synthesis

Perbromoalkylphenols :

680 mmol (35 ml) of bromine were introduced over a period of 5 hours into a suspension of 150 mmol of phenol and 0.5 g of iron dust in 225 ml of carbon tetrachloride. The suspension was allowed to react for 24 hours at room temperature and then heated to boiling and filtered. Perbromo alkyl phenol was crystallized out by cooling.

4-methyl-2,3,5,6-tetrabromophenol : c.y. 81 % m.p. 196°C (10) ; ^{1}HNMR : s, 2.7, 3H ; s, 6.0, 1H ; IR$_{(KBR)}$: OH 3420, C=C$_{arom.}$ 1550

2-methyl-3,4,5,6-tetrabromophenol : c.y. 84 % m.p. 204°C (10) ; ^{1}HNMR : s, 2.45, 3H ; s, 4.0, 1H; IR : OH 3460, C=C$_{arom.}$ 1530

4-ethyl-2,3,5,6-tetrabromophenol : c.y. 81 % m.p. 109°C (10) ; found C 21,3 % ; H 1,37 % (calc. 21.9 and 1.37) ; ^{1}HNMR : t, 1.13, 3H ; q, 3.18, 2H ; s, 6.1, 1H ; IR : OH 3420, C=C$_{arom.}$ 1540

Perchloroalkylphenol :

6 mmol of tetrabromoalkylphenol and 45 mmol of cuprous chloride were refluxed in 20 ml of dimethylformamide. The cooled solution was washed with ether/water and the dry organic layer was treated with carbon black and filtered. Evaporation of the filtrate gave the desired product.

4-methyl-2,3,5,6-tetrachlorophenol : c.y. 66 % m.p. 190°C (11) ; found C 34,3 % ; H 1.71 % (cal. 34.3 and 1.63) ; ^{1}HNMR : s, 2.6, 3H ; s, 6.5, 1H ; IR : OH 3500, C=C$_{arom.}$ 1540

4-ethyl-2,3,5,6-tetrachlorophenol : c.y. 59 % m.p. 76°C ; found C 36.6 ; H 2.26 (calc. 36.90, 2.30) ; ^{1}HNMR : t, 1.27, 3H ; q, 3.18, 2H ; s, 6.1, 1H ; IR : OH 3400, C=C$_{arom.}$ 1540

Cyclohexadienones

A solution containing 2.1 ml of nitric acid (d 1.52) in 10 ml of acetic acid were added over a 10 minutes period to a solution of 10 mmol halogenoalkylphenol in 30 ml of pure acetic acid at 10°C. The suspension was allowed to react for 2 hours at 5°C and precipitated by adding 30 ml of water. The crystallized products were filtered and washed with water and heptane and dried under vacuum. All products are decomposed by heating above 80°C.

4-nitro-4-methyl-2,3,5,6-tetrabromo-2,5-cyclohexadien-1-one 3 : c.y. 88 % ; ^{1}HNMR : s, 2.27, 3H ; IR : C=O 1680
6-nitro-6-methyl-2,3,4,5-tetrabromo-2,4-cyclohexadien-1-one 4 : c.y. 52 % ; IR : C=O 1675
4-nitro-4-ethyl-2,3,5,6-tetrabromo-2,5-cyclohexadien-1-one 5 : c.y. 90 % ; ^{1}HNMR : t, 0.77, 3H ; q, 2.82, 2H ; IR : C=O 1685
4-nitro-4-methyl-2,3,5,6-tetrachloro-2,5-cyclohexadien-1-one 6 : c.y. 90 % ; ^{1}HNMR : s, 2.2, 3H ; IR : C=O 1680
4-nitro-4-ethyl-2,3,5,6-tetrachloro-2,5-cyclohexadien-1-one 7 : c.y. 73 % ; ^{1}HNMR : t, 0.9, 3H ; q, 2.9, 2H ; IR : C=O 1690

Starting materials :

Hydroxy naphthalenes were obtained from Janssen Chimica : methoxy hydroxy naphtalenes were prepared by alkylation with dimethyl sulfate (12) ; 1-acetoxy-5-hydroxy naphthalene was prepared from 1,5-dihydroxynaphthalene.

1,5-diacetoxy naphthalene

40 mmol (6.4 g) of 1,5-dihydroxy naphthalene were mixed with 60 ml of pyridine and 89 mmol (6.4 ml) of acetylchloride were slowly dropped into this mixture (T < 40°C). The solution was then left to react overnight and precipitated with 100 ml water. The 1,5-diacetoxy naphthalene precipitate was filtered, washed with water and dried in an oven at 60°C.
Yields : 8.6 g (88 %) m.p. 166°C of product with correct analysis (13).

5-acetoxy-1-hydroxy naphthalene

6 mmol (1.46 g) 1,5-diacetoxy naphthalene and 6 mmol (0.96 g) of 1,5-dihydroxy naphthalene were added to 50 ml of toluene and 1.1 mmol of sodium methoxide were added to this suspension which was refluxed for 72 hours. The precipitate was filtered and recrystallized in a chloroform/hexane mixture after cooling.
Yield 1.43 g (60 %) ; m.p. 156°C ; found % C 71.19 ; H 5.04 ; (calc % : C 71.29 ; H 4.95) ; ^{1}HNMR : 8.25, dd, 1H ; 7.45, t, 1H ; 7.4, t, 1H ; 7.28, dd, 1H ; 6.93, m, 1H ; 2.42, s, 3H ; IR : OH 3440 ; C=C$_{arom}$ 1600 ; C=O 1730.

Nitration using nitric acid

7 mmol of 100 % nitric acid (d ≈ 1.52) in 10 ml of acetic acid were added to a solution of naphthol in 20 ml of acetic acid at 5°C. After 2 hours at 5°C, the dark suspension was washed with CH_2Cl_2/water, dried and evaporated. The nitro products were titrated by HPLC (SiO_2/heptane-ethylacetate) using benzene as internal standard and by ^{1}HNMR using tetrachlorethane as internal standard.

Nitration using nitrocyclohexadienones

5 mmol of nitrocyclohexadienones were added to 5 mmol of substrate in 40 ml of dry ether. The reaction was allowed to react for 2 hours at room temperature. The solution was evaporated under vacuum and the crude product was titrated by HPLC and NMR as above.

Separation and purification

The crude products were added to 20 ml of methanol/water (80/20) and the perhalogenophenols were filtered and washed with the same solvent. The latter can be used for reagent preparation without any further purification (recovery yield : 80 %). The solution was then evaporated under vacuum and the crude nitro products were purified by chromatography (SiO_2/heptane-ethylacetate). Isolated yields : 80 to 90 % of the weight of products determined by titration. The by-products are a brown mixture of various oxidized compounds.

2-nitro-1-naphtol 9 (17) ; 4-nitro-1-naphtol 10 (13) ; 1-nitro-2-naphthol 11 (14) have physical characteristics identical to those reported in the literature.

1-nitro-2,7-dihydroxynaphthalene 12 : m.p. 196°C (litt. 198° (15)) ; found % : C 58.33, H 3.34, N 6.53 ; (Calc. % 58.5, 3.4, 6.8) ; ^{1}HNMR : 8.77, d, 1H ; 7.86, d, 1H ; 7.76, d, 1H ; 7.4, dd, 1H ; 6.97, d, 1H ; IR : OH 3430 ; C=C$_{arom}$ 1590 ; NO_2 1520.

2-nitro-1,7-dihydroxynaphthalene 13 : m.p. 220° C ; found % : C 58.3, H 3.4, N 6.7 ; (Calc. % : 58.5, 3.4, 6.8) ; ^{1}HNMR : 7.87, d, 1H ; 7.78, d, 1H ; 7.38, dd, 1H ; 7.34, d, 1H ; IR : OH 3390 ; C=C$_{arom}$ 1600, 1580 ; NO_2 1580, 1360.

4-nitro-1,7-dihydroxynaphthalene 14 : m.p. > 250°C ; found % : C 58.57, H 3.15, N 6.35 ; (Calc. % : 58.5, 3.4, 6.8) ; ^{1}HNMR : 8.77, d, 1H ; 8.26, d, 1H ; 7.76, d, 1H ; 7.4, dd, 1H ; 6.88, d, 1H ; IR : OH 3260 ; C=C$_{arom}$ 1600, 1580 ; NO_2 1550, 1340.

1-nitro-2,6-dihydroxynaphthalene 15 : m.p. 173°C ; found % : C 58.8, H 3.36, N 6.36 ; (calc. % : 58.5, 3.4, 6.8) ; ^{1}HNMR : 8.64, d, 1H ; 7.84, d, 1H ; 7.32, dd, 1H ; IR : OH 3340 ; C=C$_{arom}$ 1610 ; NO_2 1550, 1340.

2-nitro-1,4-dihydroxy benzene 16 : m.p. 133°C (litt. 132°C (16)) ; ^{1}HNMR (CD_3OD) : 7.21, dd, 1H ; 7.20, d, 1H ; 7.06, d, 1H ; IR : OH 3430 ; C=C$_{arom}$ 1590 ; NO_2 1520.

2-nitro-1,5-dihydroxynaphthalene 17 : m.p. 226°C ; found % : C 58.53, H 3.27, N 6.54 ; (Calc. % : 58.5, 3.4, 6.8) ; ^{1}HNMR : 8.04, d, 1H ; 7.94, d, 1H ; 7.77, d, 1H ; 7.5, t, 1H ; 7.5, t, 1H ; 7.15, d, 1H ; IR : OH 3200, 3340 ; C=C$_{arom}$ 1750, 1580 ; NO_2 1520, 1360.

4-nitro-1,5-dihydroxynaphthalene 18 : m.p. 187°C ; found % : C 58.56, H 3.42, N 6.55 ; (Calc. % : 58.5, 3.4, 6.8) ; ^{1}HNMR : 7.98, dd, 1H ; 7.59, d, 1H ; 7.5, t, 1H ; 7.05, dd, 1H ; 6.85, d, 1H ; IR : OH 3200, 3340 ; C=C$_{arom}$ 1590, 1600 ; NO_2 1520, 1360.

2-nitro-5-methoxy-1-hydroxynaphthalene 19 : m.p. 152°C ; found % : C 59.94, H 3.84, N 6.77 ; (Calc. % : 60.27, 4.1, 6.39) ; ^{1}HNMR : 8.1, d, 1H ; 8.0, d, 1H ; 7.77, d, 1H ; 7.57, t, 1H ; 7.11, d, 1H ; 4.0, s, 3H ; IR : OH 3440 ; C=C$_{arom}$ 1595 ; NO_2 1515, 1350.

4-nitro-5-methoxy-1-hydroxynaphthalene 20 : m.p. 165°C ; found % : C 60.87, H 3.73, n 6.23 ; (Calc. % : 60.27, 4.1, 6.39) ; ^{1}HNMR : 7.95, d, 1H, 7.5, t, 1H ; 7.45, d, 1H ; 7.05, d, 1H ; 6.82, d, 1H, 3.9, s, 3H ; IR : OH 3340 ; C=C$_{arom}$ 1595 ; NO_2 1515, 1350.

1-nitro-2-hydroxy-3-methoxy naphthalene 21 : m.p. > 250°C ; found % : C 60.0, H 4.14, N 6.15 ; (Calc. % : 60.27, 4.1, 6.39) ; ^{1}HNMR : 8.53, dd, 1H, 7.63, t, 2H ; 7.62, dd, 1H ; 7.33, s, 1H ; 4.02, s, 3H ; IR : OH 3440 ; C=C$_{arom}$ 1595 ; NO_2 1375, 1515.

1-nitro-2-hydroxy-7-methoxy naphthalene 22 : m.p. 130°C ; found % : C 59.97, H 4.07, N 5.96 ; (Calc. % : 60.27, 4.1, 6.39) ; ^{1}HNMR : 8.4, d, 1H ; 7.88, d, 1H ; 7.69, d, 1H ; 7.1, d, 1H ; 7.06, d, 1H ; 3.88, s, 3H ; IR : OH 3450 ; C=C$_{arom}$ 1620 ; NO_2 1530, 1370.

1-nitro-2-hydroxy-6-methoxy naphthalene 23 : m.p. > 250°C ; found % : C 60.1, H 4.0, N 6.3 ; (Calc. % : 60.27, 4.1, 6.39) ; ^{1}HNMR : 8.84, d, 1H ; 7.9, d, 1H ; 7.37, dd, 1H ; 7.24, d, 1H ; 7.16, d, 1H ; 3.98, s, 3H ; IR : OH 3450 ; C=C$_{arom}$ 1610 ; NO_2 1520, 1380.

2-nitro-5-acetoxy-1-hydroxynaphthalene 24 : ^{1}HNMR : 8.48, dd, 1H ; 7.6, m, 2H ; 7.45, d, 1H ; 2.47, s, 3H ; IR : OH 3440 ; C=O 1760 ; C=C$_{arom}$ 1590 ; NO_2 1530.

4-nitro-5-acetoxy-1-hydroxy naphthalene 25 : ^{1}HNMR : 8.32, dd, 1H ; 7.62, d, 1H ; 7.6, t, 1H ; 7.42, dd, 1H ; 6.84, d, 1H ; 2.33, s, 3H ; IR : OH 3440 ; C=O 1745 ; C=C 1590 ; NO_2 1530.

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