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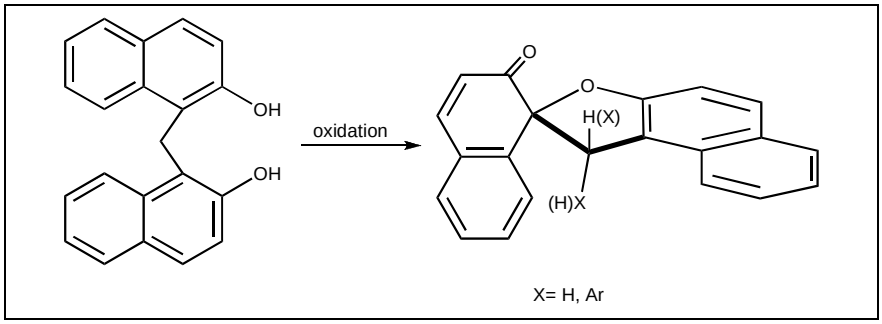

Bis(2-hydroxy-1-naphthyl)methane derivatives have been efficiently converted to their corresponding spirans through three methods, *i.e.* oxidation by TCCA under mild reaction conditions, Ph_3Bi catalyzed air oxidation, and by electrochemical reaction. The first two methods are diastereoselective and give either of the two possible diastereomers, while the electrochemical method produces equal amounts of these diastereomers.

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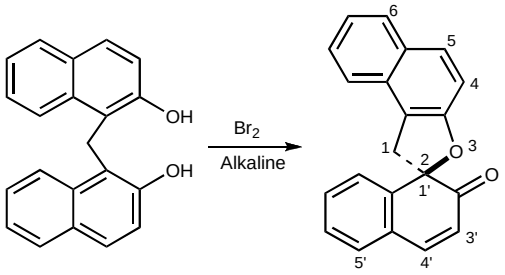
INTRODUCTION

The mild alkaline oxidation of bisnaphthols was reported by Abel in 1892 [1]. The product was believed to be a peroxide, but on the basis of chemical evidence the spirodienone structure **2** was later reassigned to it [2,3].

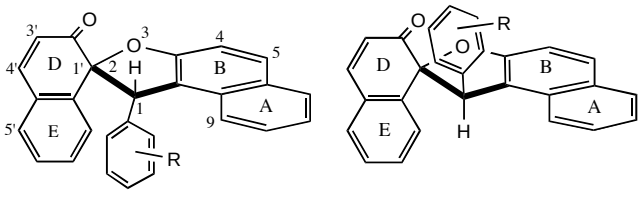


1 **2**

The spirodienone derivatives of substituted and unsubstituted bis(naphthol)methanes have been the subject of numerous studies and remain one of the most thoroughly studied members of the spirodienone family [4-17]. The Abel's ketone **2** was also prepared by oxidizing **1** with $NaBiO_3$ in refluxing benzene in 3 hours [18].

Oxidation of bis(2-hydroxy-1-naphthyl)methane **1** with *o*-chloranil [tetrachloro-*o*-benzoquinone] was studied by Kasturi and coworkers in 1979 who obtained five products [19]. The reaction of the substituted bisnaphthols with DDQ has been also carried out in refluxing dry benzene yielding the corresponding spiro compounds along with dimerized products [5].

According to Kasturi's reports, Abel ketone derivatives have two sets of diastereomers **3** and **4**; the stereoisomer **4** is formed when steric hindrance is the decisive factor. By their procedure, the use of more than one molar equivalent of persulphate or freshly prepared solution of potassium hypobromite (from bromine in 10% Aq. KOH at 0 ºC) gives **3**, whereas iodine oxyacids and (diacetoxyiodo) benzene are specific for the preparation of **4** in refluxing benzene. Radical type oxidants such as hexacyanoferrate (III) (in benzene and pyridine) and 2,4-di-*t*-butyl-6-phenylphenoxyl give mixtures of **3** and **4** [13,20]. The two diastereomers are distinguished by the fact that isomers of series **3** show in their ^1H NMR a doublet near δ 6.1 ppm (vinylic H-3'); while for isomers of series **4**, this hydrogen appears at about δ 5.4 ppm; the up-field shift being due to the shielding effect of the phenyl ring [13].



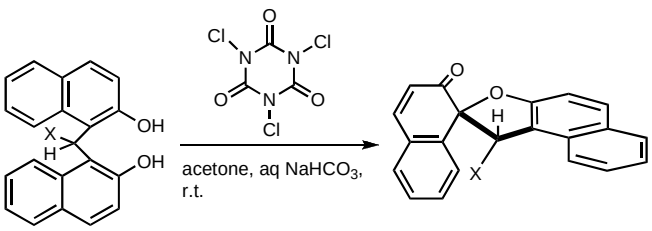
3 **4**

As is evident from the above mentioned examples, the oxidizing agents and/or solvents are toxic, and carcinogenic (like benzene). Therefore, following the general trend toward green chemistry, we now report three ways for the oxidation of bisnaphthols which are presented in three parts. In part 1, the diastereomers of

series **3** are formed by the action of TCCA in acetone solution. In part 2, the catalytic action of Ph_3Bi on air-oxidation of bisnaphthols is presented. And finally, it is shown that electro-oxidation of bisnaphthols gives a 1:1 mixture of the two diastereomeric seris **3** and **4**.

Part 1. Oxidation of bisnaphthols by TCCA. This part describes the efficient diastereoselective oxidation of bisnaphthols to **3**, under mild reaction conditions (in acetone without adding any catalyst) using less than one molar equivalent of TCCA [1,3,5-trichloro-1,3,5-triazin-2,4,6-(1*H*,3*H*,5*H*)-trione] (Scheme 1). Notably TCCA is a relatively stable and very cheap reagent that has been used synthetically in oxidation and chlorination of various types of compounds [21,22]. (In many reported methods TCCA has been used with combination of different catalysts *e.g*. $RuCl_3$ and Tempo for oxidation reaction or using metal halide such as NaBr [23,24].)

Scheme 1



1, X= H
1a, X= C_6H_4
1b, X=4-$CH_3C_6H_4$
1c, X= 3-$CH_3C_6H_4$
1d, X= 4-ClC_6H_4
1e, X= 2-ClC_6H_4
1f, X= 4-BrC_6H_4
1g, X= 3-BrC_6H_4
1h, X= 4-$CH_3OC_6H_4$

2, X= H
3a, X= C_6H_4
3b, X=4-$CH_3C_6H_4$
3c, X= 3-$CH_3C_6H_4$
3d, X= 4-ClC_6H_4
3e, X= 2-ClC_6H_4
3f, X= 4-BrC_6H_4
3g, X= 3-BrC_6H_4
3h, X= 4-$CH_3OC_6H_4$

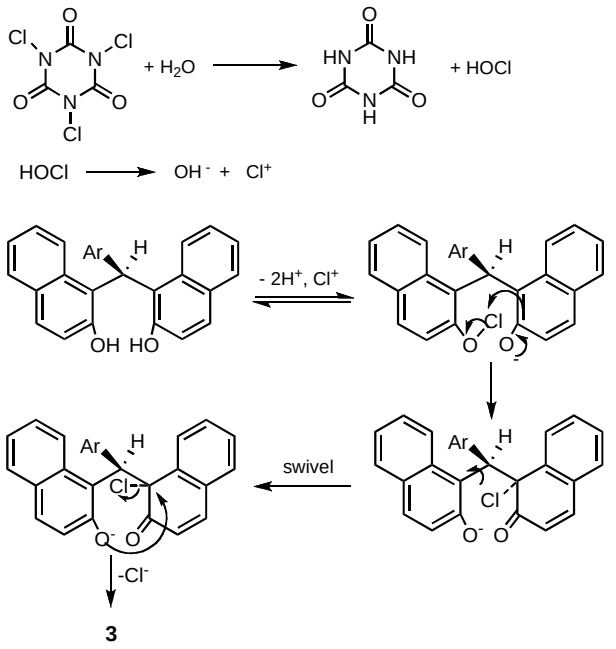
Our general procedure is based on the addition of TCCA/acetone solution to a slightly alkaline aqueous acetone solution of bisnaphthols at room temperature without any catalyst or metal halide. The conversion of all tested substrates is 100% and the oxidation reaction is practically quantitative (Table 1).

Table 1: Reaction time, yield and melting point of products shown in Scheme 1.

Entry	Product	Time (min)	Yield (%)	M.P. (Lit) ºC
1	**2**	1.5 h	85	170-171 (168-169) [1]
2	**3a**	30	87	210-211
3	**3b**	10	84	198-200
4	**3c**	10	83	187-188
5	**3d**	5	95	262-263
6	**3e**	30	81	259-260
7	**3f**	4	81	214-216
8	**3g**	3	79	204-205
9	**3h**	5	92	199-200 (195-197) [12]

Inspection of spectral data (which we will focus, throughout this paper merely on ^{1}H NMR spectra because Abel's ketones are fairly known compounds) shows that the chemical shift of H-3' of all substituted products appears at 6.2-6.3 ppm, which is a proof for the formation of diastereomers series **3**. To account for such a diastereoselectivity a plausible reaction mechanism is shown in Chart 1.

Chart 1

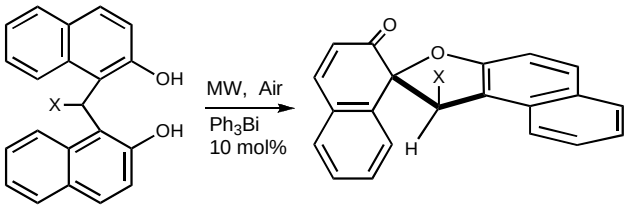


The reaction is reasonably fast, and only in one case, *i.e*. entry 1, it requires 1.5 h for completion. During the reaction, TCCA is converted into cyanuric acid (CAN) with the generation of HCl, which is neutralized with an acid scavenger such as pyridine, K_2CO_3, NaOH and $NaHCO_3$ [25,26]. In the present oxidation reaction, aqueous $NaHCO_3$ solution was used for the reaction to proceed under mild conditions with very good to excellent yields.

Part 2. Ph_3Bi catalyzed air-oxidation of bisnaphthols under microwave irradiation. Postel and Duñach in a review have mentioned the catalytic activity of Bi(III) compounds, such as triphenylbismuth and Bismuth(III) mandalate, in certain oxidation reactions [27]. Therefore we concluded that Ph_3Bi might be a good catalyst for the oxidation of bis(naphthol)methanes in the presence of oxygen. Following these lines and considering the low toxicity of bismuth compounds we report the synthesis of Abel's ketone and its derivatives by air oxidation of the corresponding bis(naphthol)methanes **1**, **1a-b**, **1d-e** and **1h** in the presence of a catalytic amount of Ph_3Bi [10 mol%] (Scheme **2**). This reaction may be carried out under microwave irradiation without the *need* of alkaline medium. Appearance of hydrogen number 3' of all

products at 5.2-5.5 ppm range in the ^{1}H NMR spectra is a proof for the formation of diastereoisomer series **4**.

Scheme 2



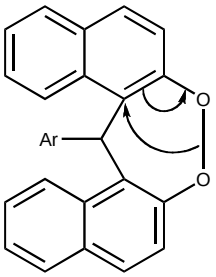
1, X= H
1a, X=C_6H_5
1b, X=4-$CH_3C_6H_4$
1d, X=4-ClC_6H_4
1e, X=2-ClC_6H_4
1h, X=4-$CH_3OC_6H_4$

2, X=H
4a, X=C_6H_5
4b, X=4-$CH_3C_6H_4$
4d, X=4-ClC_6H_4
4e, X=2-ClC_6H_4
4h, X=4-$CH_3OC_6H_4$

Table 2: Reaction time, crude yield and melting point of products shown in Scheme 2

Entry	Product	Time (min)	Yield (%)	M.P. (Lit) ºC
1	**2**	12	98	170-171 (168-169) [1]
2	**4a**	14	85	263-264
3	**4b**	10	68	227-229
4	**4d**	15	70	262-263
5	**4e**	5	72	259-260
6	**4h**	14	83	217-220 (227-229) [1]

It should be mentioned that, when acetone solutions of halo-compounds such as **1d** and **1e** stand for a relatively long time, they are oxidized to **4d** and **4e** respectively. Therefore, it seems that these two processes, *i.e.* sluggish oxidation of halo-compounds in acetone solution and relatively fast Ph_3Bi catalyzed oxidation of all bisnaphthols may have the same peroxide intermediate **5**. The stereo-view of such an intermediate (from AM1 calculations) for the oxidation of **1a** to **4a** is presented below (see Figure 1).



5

Inspection of this molecular model reveals that, of the two conformations which would allow the attack of one or the other oxygen on the phenyl ring to form the five-membered heterocyle, the conformation shown in Figure 1

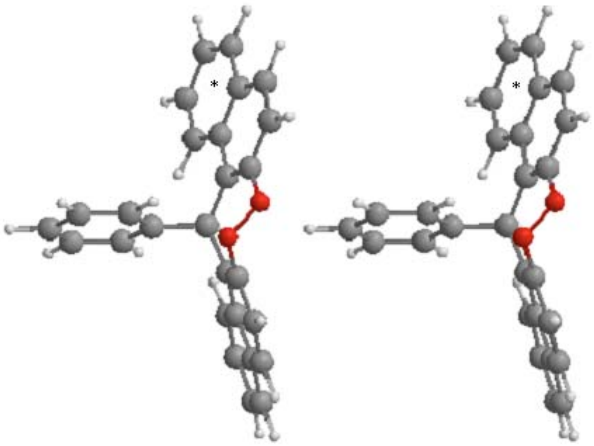


Figure 1: Stereo-view of peroxide intermediate

is the highly preferred one because there is much less steric hindrance between the starred ring and the μ-phenyl ring. In that conformation, only the peroxydic oxygen the further away form the μ-phenyl ring has the proper orientation to form the spiro diastereoisomer **4a**.

To prove the identity of the reaction product, we have succeeded in preparing single crystals for one of the compounds (**4h**) and fully characterized its structure by X-ray. Figure 2 shows the shape and Tables 3 and 4 present selected internal parameters of the compound **4h**.

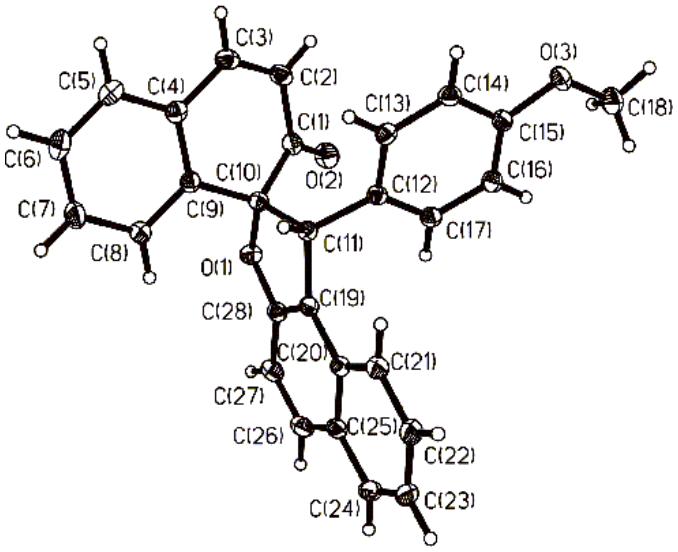


Figure 2: X-ray (ORTEP) of compound **4h**.

Part 3. Electro-oxidation of bisnaphthols. Cyclic voltammograms of bisnaphthols (1.0 mM) in a solution containing sodium hydrogen carbonate buffer (0.20 *M*, pH 8.3), show an anodic peak at 0.38-0.52 V but no corresponding cathodic peak even at a scan rate of 1000

Table 3: Selected bond lengths (Å) for compound **4h**

O(1)-C(28)	1.3675(13)	C(1)-C(2)	1.4630(16)	C(3)-C(4)	1.4625(16)	C(11)-C(19)	1.5107(14)
O(1)-C(10)	1.4439(13)	C(1)-C(10)	1.5284(15)	C(9)-C(10)	1.5120(15)	C(19)-C(28)	1.3655(15)
O(2)-C(1)	1.2190(14)	C(2)-C(3)	1.3408(17)	C(10)-C(11)	1.6146(15)		

Table 4: Selected bond angles (degree) of compound **4h**

C(28)-O(1)-C(10)	108.18(8)	C(9)-C(10)-C(1)	113.04(9)	C(28)-C(19)-C(11)	109.97(9)
O(2)-C(1)-C(2)	123.01(10)	O(1)-C(10)-C(11)	106.65(8)	C(20)-C(19)-C(11)	130.22(10)
C(2)-C(1)-C(10)	116.41(9)	C(1)-C(10)-C(11)	109.54(8)	C(19)-C(28)-O(1)	114.50(9)
C(3)-C(2)-C(1)	120.60(10)	C(19)-C(11)-C(12)	115.52(9)	O(1)-C(28)-C(27)	121.72(10)
O(1)-C(10)-C(9)	109.37(8)	C(19)-C(11)-C(10)	99.73(8)		
O(1)-C(10)-C(1)	108.09(8)	C(12)-C(11)-C(10)	115.45(8)		

mVs^{-1} (see Figures 3 and 4). Therefore, the oxidation is irreversible due to the rapid follow up chemical reactions as discussed below in presenting the results of preparative oxidation. [Controlled potential coulometry also performed in a divided cell under the above conditions].

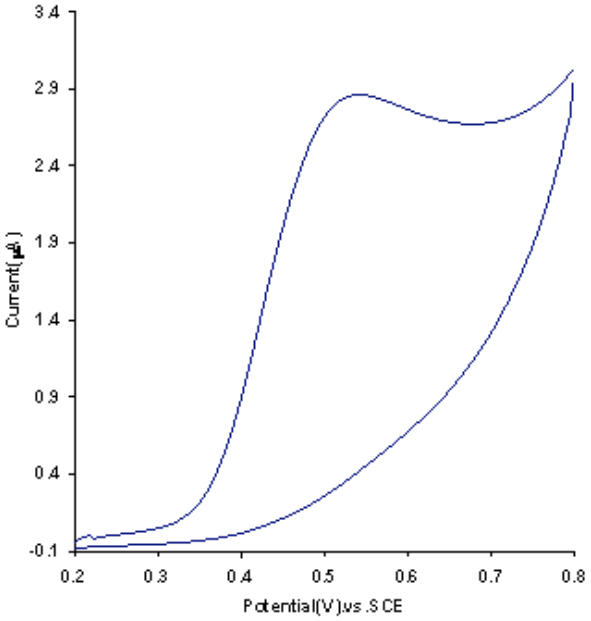


Figure 3. voltamogram of *p*-methoxybisnaphthol **1h** at a glassy carbon electrode (1.8mm diameter) in solution containing 0.20 M carbonate buffer (pH 8.3). Scan rate: 20 mVs^{-1}; t=25±1 ºC.

The yields, the quantity of coulombs passed, and the required time for the electro-oxidation of bisnaphthols **1a**, **1b**, **1c**, and **1h** are presented in Table 5. There are no data for chloro- and bromosubstituted bisnaphthols **1d**, **1e**, and **1f**. This is because these compounds are air-oxidized to their corresponding diastereoisomers **4d**, **4e** and **4f**. Therefore, the diastereomeric ratio would not be representative of that of the electro-oxidation.

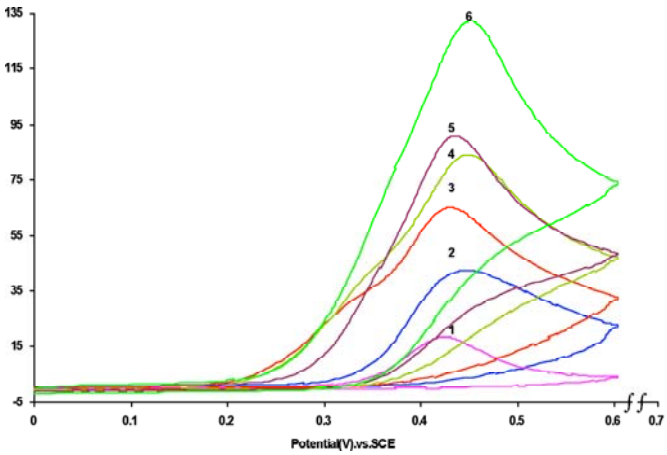


Figure 4. Typical cyclic voltammograms of 1mM *p*-methylbisnaphthol (**1b**) in 50:50 water/acetonitrile solution at various scan rates. Scan rates from (1) to (6) are: 100, 200, 300, 400, 500, and 1000 mVs^{-1}, respectively, at a glassy carbon electrode (1.8 mm diameter) in solution containing 0.20 M carbonate buffer (pH 8.3). *t*=25±1 ºC.

Table 5: Reaction time and crude yields of electro-oxidation products

Entry	Product	Time (h)	Yield (%)
1	**2**	22.58	83
2	**3a-4a**	22.58	90
3	**3b-4b**	23	75
4	**3c-4c**	16	92
5	**3h-4h**	21.88	94.5

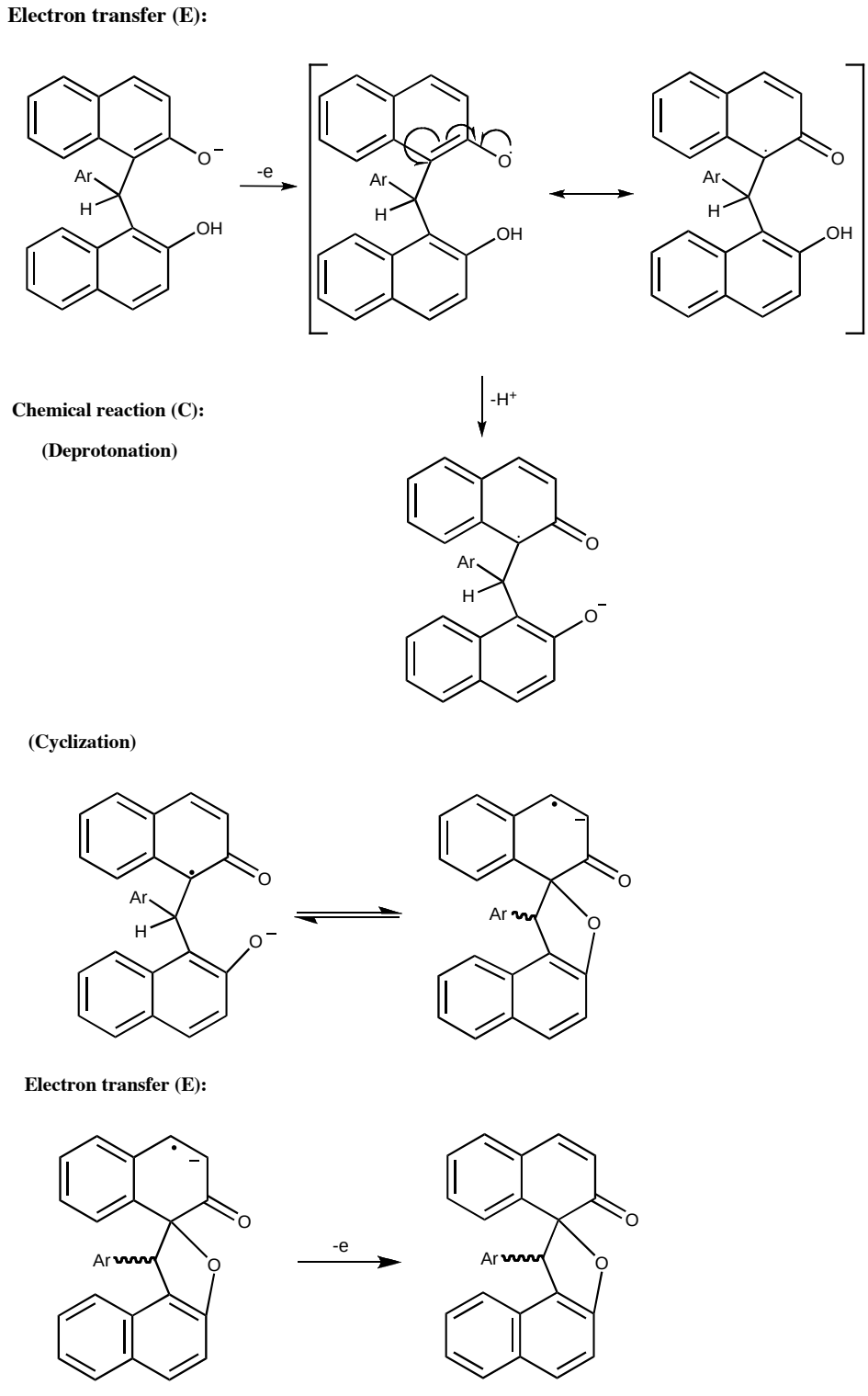
Calculations, based on consumed coulombs, reveals that in electro-oxidation reaction two electrons are exchanged. The formation of a diradical by a two-electron oxidation is rejected because it may lead to the peroxide intermediate mentioned in Part 2, which will be in favor of diastereomers of series **4**. Therefore, to account for the formation of a 1:1 ratio of distereomeres **3** and **4**, an **ECE** mechanism is proposed (Chart 2). The first step, after deprotonation reaction at pH 8.3, is an electro-oxidation reaction (electron transfer, **E**). This step is followed by

two chemical reactions (**C**), *i.e*. deprotonation and cyclization. As there is no preference for the cyclization reaction, it will lead to the formation of the two diastereomers in a 1:1 ratio. The final step (**E**) is a fast one-electron oxidation of the radical anion.

CONCLUSION

The oxidation of each substituted bisnaphthol by TCCA gives only one product the 3'H of which appears (in the ^{1}H NMR spectrum) at about δ 6.2 ppm. In this case

Chart 2



therefore, the diastereomer **3** is formed. On the other hand, when the same bisnaphthols are oxidized in the presence triphenylbismuth (10 mol %), the above said hydrogen appears now at about δ 5.2 ppm, which is representative of diastereomer series **4**. However, the electro-oxidation of bisnaphthols shows, for each corresponding ^{1}H NMR spectrum of the product, a set of two doublets at about δ 6.2 ppm and δ 5.5 ppm. The 1:1 integral ratio of these two hydrogens is a good evidence of the non-selectivity of electro-oxidation reaction.

In conclusion, we have run the oxidation of bisnaphthols by using TCCA, air, or electricity. In the first case, the reaction conditions are mild, safe, and the separation procedure is easy to perform. In the second case, the reaction proceeds under environmental friendly and solvent free conditions: microwave irradiation of the molten reactants mixture and use of a relatively benign catalyst, Ph_3Bi. The last method of oxidation, *i.e*. electro-oxidation reaction, is both safe and clean. From the point of view of green chemistry, use of the electrosynthesis method has some important advantages. Clean synthesis, use of electricity as energy instead of oxidative reagents, use of aqueous/organic media instead of organic solvents, one-step room temperature reaction and, technical feasibility are among the advantages to be mentioned.

EXPERIMENTAL

All solvents and reagents were used as obtained from Merk (except that of TCCA which was purchased from Fluka). The methylenbisnaphthol **1** was prepared according to the Mironov method and the other substrates, **1a-1h**, by the procedure of Hewitt and Tunner [28-29]. Standard NMR spectra were obtained on a Brüker 500 MHz (and/or Jeol 90 MHz) spectrometers, respectively in $CDCl_3$ as solvent. Melting points were determined by electrothermal melting point apparatus without further correction. The source of microwave radiation was the LG domestic microwave oven (model MG-583MC). In electro-oxidation experiments an auto lab potentiostat/ galvanostat (Model BHP2050, by Behpajooh Co., Iran) was used. The working electrode was an assembly of four graphite rods (6mm diameter and 4 cm length) and a graphite rod constituted the counter electrode. The working electrode potentials were measured versus SCE (all electrodes were purchased from AZAR ELECTRODE, Iran).

General Procedures.

Oxidation by TCCA. The procedure for the oxidation of 4-methylbisnaphthol (entry 3 Table 1) is representative for all cases. An aqueous 15% solution of $NaHCO_3$ (3 mL) was added to the bisnaphthol (0.0406 g, 0.1 mMol) in acetone (10 mL), stirred and maintained at 0 ºC; TCCA (0.0176 g, 0.075 mMol) in acetone (2 mL) was then slowly added within 15 min (When it was added at once, side products were formed and no attempt was made to identify them) at 0 ºC. The color of the white suspension rapidly changes to yellow. After addition of TCCA solution, the mixture was warmed to room temperature and stirred for the required time until completion (monitored by TLC). The mixture was then filtered and concentrated under vacuum. The aqueous phase was washed with portions of AcOEt, treated with 1 *N* HCl, and extracted twice with AcOEt. The organic layer was dried over Na_2SO_4 and the solvent evaporated to yield the product. Further purification was carried out by crystallization in acetone/*n*-hexane.

Ph_3Bi catalyzed air oxidation under microwave irradiation. The corresponding bisnaphthol (0.3 mMol) and triphenylbismuth (10 mol %) were mixed thoroughly and subjected to microwave irradiation under combin1 mode (20% microwave and 80% grill) for 10-14 min. in solvent free conditions. This mode was chosen to fuse the starting materials by preheating the mixture. $CHCl_3$ (5-10 mL) was added to the cooled product and the mixture was filtered. The main products were separated by column chromatography using silica gel as stationary phase and a mixture of acetone/*n*-hexane as eluent.

Electro-oxidation of bisnaphthols. A solution of sodium hydrogen carbonate buffer (40 mL) (c = 0.20 *M*, pH 8.3) in water mixed with a solution of acetonitrile (40 mL) containing bisnaphthols (1 mMol), was electro-oxidized in an undivided cell equipped with a graphite anode (an assembly of four rods, 6 mm diameter and 4 cm length) and a graphite cathode with 1 cm diameter at 40°C under constant-potential of 0.4-0.5 V. The quantity of the electricity passed was determined by a potentiostat. The process was interrupted during the electro-oxidation, and the graphite anode was washed in acetone in order to reactivate it. At the end of reaction and evaporation of acetonitrile, the solution was extracted by AcOEt, and dried over magnesium sulfate. In order to eliminate any by-product, a chromatographic step was performed and the spiran fractions re-combined for further analysis by ^{1}H NMR spectroscopy. (Because Abel's ketones are well known compounds only their NMR data are presented below)

Spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho[2,1-*b*]fur-an}-2-one. (Abel's ketone **2**); selected ^{1}H NMR ($CDCl_3$, TMS): δ3.50 (1H, d, J=15.6 Hz); δ4.06 (1H, d J=15.6 Hz); δ6.24 (1H, d, J=10.0 Hz due to hydrogen number 3'); δ 7.24-7.88 (11H, aromatic and hydrogen number 4').

1'-Phenyl-spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho-[2,1-*b*]-furan}-2-one (**3a**). ^{1}H NMR ($CDCl_3$, TMS): δ5.39 (1H, s, hydrogen number 1), δ6.27 (1H, d, J=10.0 Hz due to hydrogen number 3'), δ6.93-7.94 (16H, aromatic and hydrogen number 4').

1'-(4-Methylphenyl)-spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho[2,1-*b*]furan}-2-one (**3b**). ^{1}H NMR ($CDCl_3$, TMS): δ2.12 (3H, s), δ5.36 (1H, s, hydrogen number 1), δ6.26 (1H, d, J=9.9 Hz due to hydrogen number 3'), δ6.67-7.93 (15H, aromatic and hydrogen number 4').

1'-(3-Methylphenyl)-spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho[2,1-*b*]furan}-2-one (**3c**). ^{1}H NMR ($CDCl_3$, TMS): δ2.01 (3H, s), δ5.34 (1H, s, hydrogen number 1), δ6.25 (1H, d, J=9.90 Hz due to hydrogen number 3'), δ6.75-7.93 (15H, aromatic and hydrogen number 4').

1'-(4-Chlorophenyl)-spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho[2,1-*b*]furan}-2-one (**3d**). ^{1}H NMR ($CDCl_3$, TMS): δ5.36 (1H, s, hydrogen number 1); δ6.26 (1H, d, J=9.90 Hz due to hydrogen number 3'); δ6.86-7.94 (15H, aromatic and hydrogen number 4').

1'-(2-Chlorophenyl)-spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho[2,1-*b*]furan}-2-one (**3e**). ^{1}H NMR ($CDCl_3$, TMS): δ6.00(1H, s, hydrogen number 1); δ6.23 (1H, d, J=10.0 Hz due to hydrogen number 3'); δ6.52-7.84 (15H, aromatic and hydrogen number 4').

1'-(4-Bromophenyl)-spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho[2,1-*b*]furan}-2-one (**3f**). ^{1}H NMR ($CDCl_3$, TMS): δ5.34 (1H, s, hydrogen number 1); δ6.26 (1H, d, J=10.0 Hz due to hydrogen number 3'); δ7.00-7.94 (15H, aromatic and hydrogen number 4').

1'-(3-Bromophenyl)-spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho[2,1-*b*]furan}-2-one (**3g**). ^{1}H NMR ($CDCl_3$, TMS): δ5.32 (1H, s, hydrogen number 1); δ6.27 (1H, d, J=10.0 Hz due to hydrogen number 3'); δ7.09-7.96 (15H, aromatic and hydrogen number 4').

1'-(4-Methoxyphenyl)-spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho[2,1-*b*]furan}-2-one (**3h**). ^{1}H NMR ($CDCl_3$, TMS): δ3.62 (3H, s), δ5.35 (1H, s, hydrogen number 1), δ6.25 (1H, d, J=10.0 Hz due to hydrogen number 3'), δ6.41-7.93 (15H, aromatic and hydrogen number 4').

^{1}HNMR Spectral data for Ph_3Bi catalyzed air oxidation under microwave irradiation.

Spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho[2,1-*b*]furan}-2-one. (Abel's ketone **2**); selected ^{1}H NMR ($CDCl_3$, TMS): δ3.50 (1H, d, J=15.6 Hz); δ4.06 (1H, d J=15.6 Hz); δ6.24 (1H, d, J=9.99 Hz).

1'-Phenyl-spiro{naphthalene-1(2H),2'(1'H)-naphtho-[2,1-*b*]-furan}-2-one (**4a**). ^{1}H NMR ($CDCl_3$, TMS): δ5.22 (1H, s, hydrogen number 1), δ5.54 (1H, d, J=9.99 Hz due to hydrogen number 3'), δ7.01-7.92 (16H, aromatic and hydrogen number 4').

1'-(4-Methylphenyl)-spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho[2,1-*b*]furan}-2-one (**4b**). ^{1}H NMR ($CDCl_3$, TMS): δ1.74 (3H, s), δ5.16 (1H, s, hydrogen number 1), δ5.55 (1H, d, J=9.81 Hz due to hydrogen number 3'), δ6.87-7.93 (15H, aromatic and hydrogen number 4').

1'-(4-Chlorophenyl)-spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho[2,1-*b*]furan}-2-one (**4d**). Selected ^{1}H NMR ($CDCl_3$, TMS): δ5.17 (1H, s, hydrogen number 1); δ5.57 (1H, d, J=10.2 Hz due to hydrogen number 3'); δ6.88-7.95 (15H, aromatic and hydrogen number 4').

1'-(2-Chlorophenyl)-spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho[2,1-*b*]furan}-2-one (**4e**). selected ^{1}H NMR ($CDCl_3$, TMS): δ5.86 (1H, s, hydrogen number 1); δ5.50 (1H, d, J=10.3 Hz due to hydrogen number 3'); δ6.66-7.92 (15H, aromatic and hydrogen number 4').

1'-(4-Methoxyphenyl)-spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho[2,1-*b*]furan}-2-one (**4h**). ^{1}H NMR ($CDCl_3$, TMS): δ3.75 (3H, s), δ5.20 (1H, s, hydrogen number 1), δ5.58 (1H, d, J=9.99 Hz due to hydrogen number 3'), δ6.72-7.91 (15H, aromatic and hydrogen number 4').

^{1}HNMR spectral data for electro-oxidation reaction.

1'-Phenyl-spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho-[2,1-*b*]-furan}-2-one (**3a** and **4a**). ^{1}H NMR ($CDCl_3$, TMS): [δ5.20 (s, 1H), δ 5.39 (s, 1H) two kinds of hydrogen number 1], [δ5.51 (d, 1H d, J=9.90 Hz), δ6.26 (d, 1H d, J=9.90 Hz two kinds of hydrogen number 3')], δ6.94-7.93 (aromatic and hydrogen number 4').

1'-(4-Methylphenyl)-spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho[2,1-*b*]furan}-2-one (**3b** and **4b**). ^{1}H NMR ($CDCl_3$, TMS): [δ2.08 (3H, s), δ2.23 (3H, s), two kinds of methyl hydrogens], [δ5.17 (s, 1H), δ 5.36 (s, 1H) two kinds of hydrogen number 1], [δ5.51 (d, 1H d, J=9.90 Hz), δ6.22 (d, 1H d, J=9.90 Hz two kinds of hydrogen number 3')], δ6.66-7.90 (aromatic and hydrogen number 4').

1'-(3-Methylphenyl)-spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho[2,1-*b*]furan}-2-one (**3c and 4c**). mp: =188-190. ^{1}H NMR ($CDCl_3$, TMS): [δ2.00 (3H, s), δ2.17 (3H, s), two kinds of methyl hydrogens], [δ5.15 (s, 1H), δ 5.33 (s, 1H) two kinds of hydrogen number 1], [δ5.51 (d, 1H d, J=9.90 Hz), δ6.23 (d, 1H d, J=9.99 Hz two kinds of hydrogen number 3')], δ6.74-7.91 (aromatic and hydrogen number 4').

1'-(4-Methoxyphenyl)-spiro{naphthalene-1(2*H*),2'(1'*H*)-naphtho[2,1-*b*]furan}-2-one (**3h** and **4h**). ^{1}H NMR ($CDCl_3$, TMS): [δ3.61(3H, s), δ3.72 (3H, s), two kinds of methoxy hydrogens], [δ5.17 (s, 1H), δ 5.35 (s, 1H) two kinds of hydrogen number 1], [δ5.55 (d, 1H d, J=10.3 Hz), δ6.24 (d, 1H d, J=10.2 Hz two kinds of hydrogen number 3')], δ6.39-7.92 (aromatic and hydrogen number 4').

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