ELSEVIER

Journal of Organometallic Chemistry 571 (1998) 1–6

Journal of Organometallic Chemistry

Reductive-alkylation and aromatic coupling reactions of 1,4-benzoquinone derivatives promoted by ethylaluminum dichloride

Vitor F. Ferreira [a], Francis J. Schmitz [b,*]

[a] *Departamento de Química Orgânica, Universidade Federal Fluminense, Niterói, Rio de Janeiro, CEP 24020-150, Brazil*
[b] *Department of Chemistry and Biochemistry, The University of Oklahoma, Norman, 73019-0370, USA*

Received 20 January 1998; received in revised form 7 July 1998

Abstract

Reactions of several substituted 1,4-benzoquinones with ethylaluminum dichloride in dichloromethane were studied. It was found that some quinones undergo a new radical aromatic coupling under these conditions, while others undergo a 1,6-reductive *O*-alkylation.

Keywords: Quinones; Reduction; Alkylation; Aluminum

1. Introduction

In the course of studies directed to shortening the synthesis of perfragilin B (**1**) [1], a metabolite isolated from the bryozoan *Membranipora perfragilis* [2,3], Lewis acid catalyzed Diels-Alder reactions of 2,3-dichloro-1,4-benzoquinone and 2-aza-1,3-bis-(*t*-butyldimethylsilyloxy)-1,3-butadiene [4] were attempted. When ethylaluminum dichloride was investigated as the catalyst no Diels-Alder product was obtained, but instead the alkoxyphenol derivative **10** was obtained in 75–85% yields (Scheme 1). The same results were obtained when the azadiene was left out of the reaction. Surprisingly, reaction of the monochlorobenzoquinone, 2-chloro-1,4-benzoquinone (**8**), with ethylaluminum dichloride afforded the phenol-dimer **20** in 61% yield (Scheme 1).

A search of the literature revealed that the reaction of alkylaluminum dichlorides with 1,4-benzoquinones had been already investigated by Pasynkiwicz [5,6] and Florjanczyk [7] who found that some chlorinated 1,4-benzoquinone derivatives undergo 1,6-addition upon reaction with alkylaluminum dichlorides (ether solvent) producing 4-alkoxyphenol analogs similar to compound **10**. However, no alkoxyphenol dimers such as **20** were reported in any of these studies.

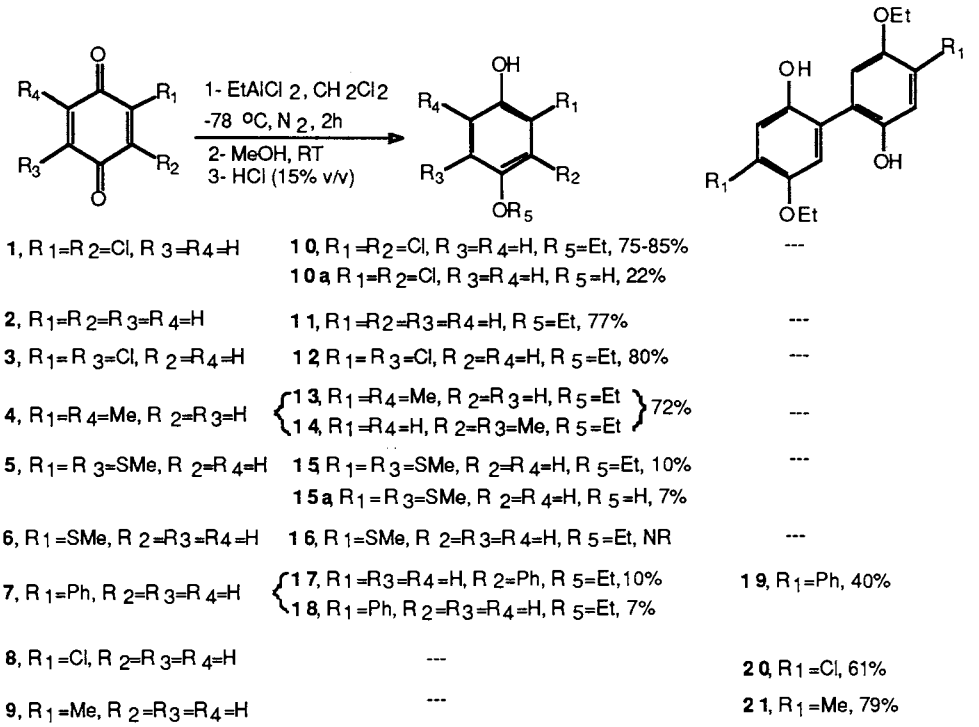
Because 4-alkoxyphenols are important starting materials in many syntheses [8–10] and their preparation is not straightforward, and because **1** and **8** gave such different types of products we decided to investigate the scope of this reaction further. In this paper we present the results of our investigation of the reductive-alkylation of variously substituted 1,4-benzoquinones with ethylaluminum dichloride.

2. Results

The reactions were carried out between 1,4-benzoquinone derivatives and two equivalents of ethylaluminum dichloride at −78°C in dichloromethane. Reactions were quenched by adding methanol at room temperature and then aqueous HCl (15%). Scheme 1 shows the benzoquinone derivatives **1**–**9** used in our investigation and the corresponding products **10**–**21** which were formed.

* Corresponding author. Tel.: +1 405 3255581; fax: +1 405 3256111; e-mail: fjschmitz@chemdept.chem.ou.edu

0022-328X/98/$ - see front matter
PII S0022-328X(98)00865-1



Scheme 1. Reactions for the preparation of compounds **10**–**21**.

As can be seen in Scheme 1 1,4-benzoquinones **1**–**4** afforded the 4-ethoxyphenol derivatives **10**–**14** in good yields and no dimeric products were detected. From benzoquinones **1** and **5**, the simple 1,6-reduction products **10a** and **15a** were also isolated in 22 and 7%, respectively. The yield of ethoxyphenol **12** was much higher than that reported by Florjanczyk [5]. This may be due either to solvent differences or the higher ratio of $EtAlCl_2$/quinone (2:1 vs 1:1) used. Attempts to use a lower ratio of $EtAlCl_2$/quinone caused a decrease in the yield of **12**. The methylthio substituted 1,4-benzoquinone **5** gave low yields of reduction products and **6** gave no reduction product.

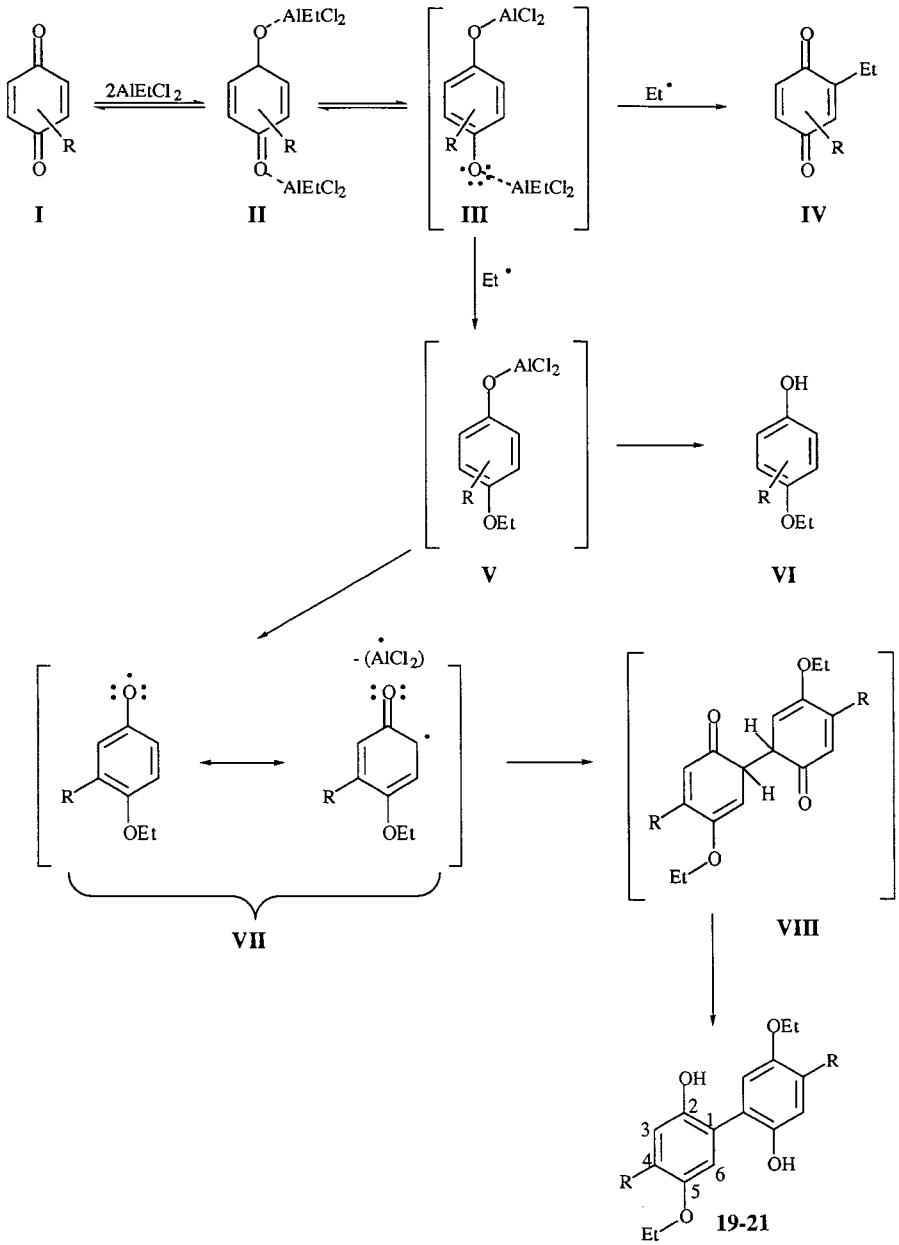
The formation of the 4-alkoxyphenols is not regioselective. No selectivity for *O*-alkylation was observed when 2,6-dimethyl-1,4-benzoquinone (**4**) was reacted; an equimolar mixture of **13** plus **14** was isolated in 72% overall yield. Also, no selectivity in the formation of the 4-ethoxyphenols **17**/**18** was observed when 2-phenyl-1,4-benzoquinone (**7**) was reacted.

When the 1,4-benzoquinone derivatives **7**–**9** were subjected to this reaction, the main products obtained were the alkoxyphenyl dimers **19**–**21**, in moderate to good yields, instead of the usual 4-alkoxyphenols.

The structures of substances **19**–**21** were determined by a combination of mass, ^{1}H- and ^{13}C-NMR spectroscopy. For **21** ($C_{18}H_{22}O_4$, HR-FAB-MS *m*/*z* 302.1510) the HMBC spectrum revealed multiple bond correlations between the aromatic methyl group (δ 2.21) and C-5, C-4 and C-3 (δ 151.6, 128.8, 118.9, respectively) while the methylene group (δ 3.95) showed a crosspeak with C-5 (δ 151.6) establishing the vicinal relationship between the methyl and ethoxy groups. Correlations were observed in the HMBC spectrum between H-3/C-1, C-2, C-4, C-5 and H-6/C-1, C-2, C-4, C-5. These correlations considered together with the absence of any observable coupling between H-6 and H-3 and lack of correlations in HMBC spectrum between H-6/C-3 and H-3/C-6 indicated that the bond between the aromatic rings occurred at position 2. The structures of **19** and **20** were assigned by comparison of their chemical shifts with those of **21**, the lack of observable coupling between the aromatic protons, and mass spectral data.

It is well known in the literature that benzoquinones can easily form persistent radical complexes containing aluminum [11,12] and other metals [13–15]. Pasynkiewicz [5] proved by ESR analysis that the conversion of **I** to **IV** and **VI** involved a radical intermediate and proposed a radical mechanism such as that shown in Scheme 2 (**III** → **IV** or **III** → **VI**).

In addition to the alkylation of oxygen by ethyl radicals observed in the present work and by earlier workers [5–7], the results with monosubstituted 1,4-benzoquinones **7**–**9** indicate that coupling between phenyl radicals also occurs to give dimeric and/or oligomeric products. The selectivity in orientation in the coupling observed for **7**–**9** suggests that the intermediate for coupling may be a mono ethylated radical such as **VII**. Dimerization of **VII** at the unhindered site



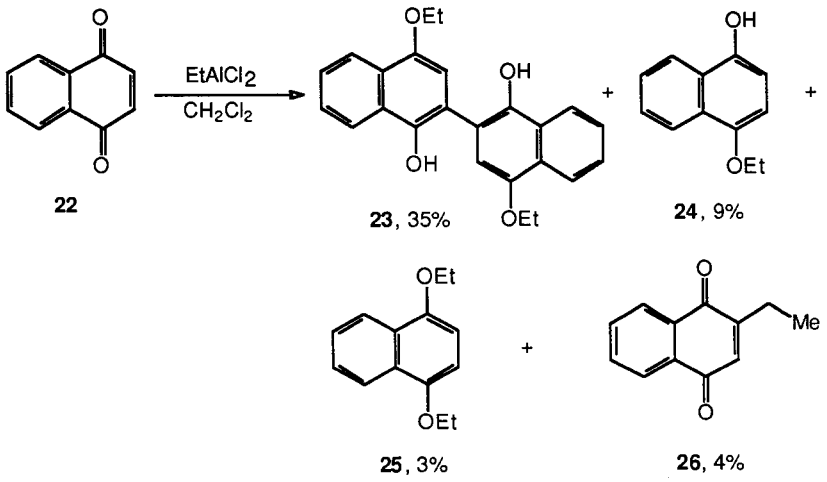
Scheme 2. Possible mechanism for the formation of substances **19**–**21.**

ortho to the oxygen radical site followed by enolization (prior to or during work up) would give the observed products. If the dimerization occurred prior to ethyl ether formation, the selective ether orientation in the dimer would be difficult to rationalize. It is not clear why the monosubstituted 1,4-quinones give dimers as major products whereas 1,4-benzoquinone itself and disubstituted 1,4-benzoquinones of various substituted patterns give predominantly 1,6-addition products.

The reaction of 1,4-naphthoquinone (**22**) with ethylaluminum dichloride has previously been investigated by Florjanczyk et al. [7] who found that 4-alkoxynaphthol **24** was formed in 26% yield along with 1,4-naphthoquinol (44%) (Scheme 3). Using our reaction conditions we obtained the 4-alkoxy dimer **23** as the major product, in addition to mono-ether **24**, di-ether **25** and C-alkylated 1,4-naphthoquinone **26** as minor components.

3. Conclusion

The present study has shown that when 1,4-benzoquinone derivatives **1**–**9** are treated with two equivalents of $EtAlCl_2$, 4-alkoxyphenols (**10**–**15**, **17**, **18**) or 4-alkoxyphenol dimers (**19**–**21**) are formed. To the best of our knowledge this is the first time that such dimers have been reported for this kind of reaction.



Scheme 3. Reaction of 1,4-naphthoquinone (**22**) with $EtAlCl_2$ in CH_2Cl_2.

4. Experimental

All solvents were redistilled. Dichloromethane was freshly distilled from calcium hydride. High resolution fast atom bombardment mass spectra (HRFABMS) were recorded in the positive ion mode on a VG ZAB-E mass spectrometer using 3-NBA matrix. Low resolution electron-impact mass spectra (12 eV) were measured on a Hewlett-Packard 5985 instrument. NMR experiments were performed on Varian XL-300, VXR-400 and VXR-500 (3 mm $^1H/^{13}C$ switchable gradient microprobe MDG-500-3) instruments; signals are reported in parts per million (ppm) referenced to the solvent used. All NMR pulse sequences were run using standard Varian software version 4.3 (HMBC, $^nJ_{CH} = 9$ Hz). IR spectra were recorded on a Bio-Rad 3240-SPC FT spectrophotometer. Freshly purified samples were used for measurement of physical constants and spectral data. The reaction mixtures were separated using preparative TLC rotors coated with silica gel in a Chromatotron model 7924 (Harrison Research Co.). Benzoquinones **2**, **4**, **7**, **8** and **9** were purchased from Aldrich. 2,3-Dichloro-1,4-benzoquinone (**1**) was prepared by the method of Norris [16] as modified by our group [17]. In this reaction benzoquinone **3** is a by product. Methylthiobenzoquinones **5** and **6** were prepared by the method of Wladislaw [18].

4.1. General procedure

To a solution of the appropriate benzoquinone derivative (1 mmol) in 5 ml of dry dichloromethane, 2 ml (two equivalents) of a solution of 1 M $EtAlCl_2$ in hexane was added dropwise under a nitrogen atmosphere over a period of 30 min at -78°C. The solution turned deep blue and was stirred at this temperature for 1 h and then for 2 h at room temperature. To this mixture, 2 ml of methanol, 10 ml of water and then 5 ml of 15% HCl (to pH ~ 6) were slowly added sequentially. The resulting gelatinous mixture was extracted with dichloromethane (3×15 ml). The resulting cloudy, organic phase was filtered through a celite column, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residues were chromatographed on silica gel columns or preparative TLC plates and eluted with a mixture of hexane:ethyl acetate (9:1).

4.2. 2,3-Dichloro-4-ethoxyphenol (*10*) and 2,3-diclorohydroquinone (*10a*)

Obtained in 75–85% yield from 2,3-dichlorobenzoquinone (**1**, 75 mg, 0.42 mmol); m.p. 74–75°C; IR (film) (ν_{max} 3370 (bs), 2987 (m), 1596 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.42 (t, 3H, $J = 7$ Hz, CH_3), 4.04 (q, 2H, $J = 7$ Hz, CH_2), 5.33 (s, 1H, OH), 6.80 (d, 1H, $J = 8.8$ Hz), 6.89 (d, 1H, $J = 8.8$ Hz); ^{13}C-NMR ($CDCl_3$) δ 14.8 (CH_3), 65.9 (CH_2), 113.4 (CH/C-5 or C-6), 113.5 (CH/C-5 or C-6), 119.9 (C-2 or C-3), 122.1 (C-2 or C-3), 146.4 (C-1), 149.4 (C-4); LRMS (12 eV) m/z (relative intensity) 206 (56), 182 (10), 180 (48), 178 (100); HRFABMS m/z 205.9871 $[M+1]^+$ ($C_8H_8O_2Cl_2$, 3.0 mmu). 2,3-Dichloro-hydroquinone (**10a**) was also obtained in 22% yield; m.p. 146–147°C; ^1H-NMR ($CDCl_3$) δ 5.24 (s, 1H, OH), 6.89 (s, 1H); LRMS (12 eV) m/z (relative intensity) 182 (10), 180 (65), 178 (100), 142 (14) 114 (9); HRFABMS m/z 177.9557 (M^+) ($C_6H_4O_2Cl_2$, 3.1 mmu).

4.3. 4-Ethoxyphenol (*11*)

Obtained in 77% yield from 1,4-benzoquinone (**2**, 120 mg, 1.10 mmol); m.p. 65–66 (lit. 65–67°C) ; ^1H-NMR ($CDCl_3$) δ 1.37 (t, 3H, $J = 7$ Hz, CH_3), 3.96 (q, 2H, $J = 7$ Hz, CH_2), 5.33 (s, 1H, OH), 6.77 (d, 1H, $J = 9$ Hz), 6.78 (d, 1H, $J = 9$ Hz); ^{13}C-NMR ($CDCl_3$) δ 14.8 (CH_3),

64.3 (CH_2), 115.7 (CH), 116.1 (CH), 119.9 (C), 149.4 (C), 152.7 (C); LRMS (12 eV) m/z (relative intensity) 138 (100), 110 (47).

4.4. 2,5-Dichloro-4-ethoxyphenol (12)

Obtained in 80% yield from 2,5-dichlorobenzoquinone (**3**, 120 mg, 0.68 mmol); m.p. 58–58°C; IR (film) (ν_{max} 3408 (bs), 1465 (s), 1201 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.42 (t, 3H, $J=7$ Hz, CH_3), 4.00 (q, 2H, $J=7$ Hz, CH_2), 5.19 (s, 1H, OH), 6.87 (s, 1H), 7.05 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ 14.6 (CH_3), 65.7 (CH_2), 114.3 (CH/C-3 or C-6), 117.6 (CH/C-6 or C-6), 117.7 (C-2 or C-5), 122.7 (C-2 or C-5), 145.4 (C-1), 148.6 (C-4); LRMS (12 eV) m/z (relative intensity) 206 (M^+, 100), 208 [$(M+2)^+$, 62], 210 [$(M+4)^+$, 11], 182 (11), 180 (59), 178 (95); HRFABMS m/z 205.9918 (M^+) ($C_8H_8O_2Cl_2$, -1.7 mmu).

4.5. 4-Ethoxy-2,6-dimethylphenol (13) and 4-ethoxy-3,5-dimethylphenol (14)

Obtained as a mixture (1:1) in 72% yield from 2,6-dimethy-1,4-benzoquinone (**4**, 136 mg, 1 mmol). ^{1}H-NMR ($CDCl_3$) δ 1.36 and 1.38 (t, $J=7$ Hz, Me), 2.10 and 2.15 (s, Me), 3.7 and 3.94 (q, $J=7$ Hz, CH_2), 6.46 (s, 1H, CH_{olefin}), 6.54 (s, 1H, CH_{olefin}).

4.6. 4-Ethoxy-2,5-di-(methylthio)phenol (15) and 2,5-di-(methylthio)hydroquinone (15a)

Obtained in 10% yield from 2,5-(methylthio)benzoquinone (**5**, 120 mg, 0.60 mmol); m.p. 73–74°C; IR (film) (ν_{max} 3400 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.42 (t, 3H, $J=7$ Hz, CH_3), 2.29 (s, 3H, SMe), 2.39 (s, 3H, SMe), 4.02 (q, 2H, $J=7$ Hz, CH_2), 6.32 (s, 1H, OH), 6.74 (s, 1H), 6.92 (s, 1H); ^{13}C-NMR ($CDCl_3$) 14.1 (SMe), 14.7 (SMe), 20.2 (Me), 65.2 (CH_2), 110.9 (CH/C-3 or C-6), 115.3 (C-2 or C-5), 148.9 (C-1), 151.1 (C-4); LRMS (12 eV) m/z (relative intensity) 230 (100), 202 (98), 201 (13); HRFABMS m/z 230.0437 (M^+) ($C_{10}H_{14}O_2S_2$, -0.2 mmu). 2,5-Di-(methylthio)-hydroquinone (**15a**) was also obtained in 7% yield; m.p. 127–129°C); IR (film) (ν_{max} 3408 (bs), 1201 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.34 (s, SMe), 6.05 (bs, OH), 7.05 (s, CH); LRMS (12 eV) m/z (relative intensity) 202 (M^+, 100), 187 (19); HRFABMS m/z 202.0119 (M^+) ($C_8H_{10}O_2S_2$, 0.3 mmu).

4.7. 4-Ethoxy-3-phenylphenol (17)

Obtained in 10% yield from 2-phenylbenzoquinone (**7**, 184 mg, 1 mmol); oil, IR (film) (ν_{max} 3420 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.39 (t, 3H, $J=7$ Hz, CH_3), 4.00 (q, 2H, $J=7$ Hz, CH_2), 4.89 (s, 1H, OH), 6.80 (bs, 1H, H-2), 6.81 (dd, $J=3$ and 9 Hz, 1H, H-6), 6.89 (d, $J=9$ Hz, 1H), 7.36–7.41 (m, 1H, Ph), 7.46–7.48 (m, 4H, Ph); ^{13}C-NMR ($CDCl_3$) δ 14.9 (Me), 64.0 (CH_2), 115.2 (CH, C-5 or C-6), 115.9 (C-5 or C-6), 116.4 (CH, C-2), 128.0 (Ph), 128.5 (C-3), 128.9 (Ph), 129.1 (Ph), 146.2 (C-1), 152.8 (C-4); LRMS (12 eV) m/z (relative intensity) 214 (100), 186 (32); HRFABMS m/z 214.0995 (M^+) ($C_{14}H_{14}O_2$, -0.1 mmu).

4.8. 4-Ethoxy-2-phenylphenol (18)

Obtained in 7.5% yield. Oil, IR (film) (ν_{max} 3413 (bs) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.28 (t, 3H, $J=7$ Hz, CH_3), 3.92 (q, 2H, $J=7$ Hz, CH_2), 4.71 (s, 1H, OH), 6.74 (d, $J=9$ Hz, 1H, H-5), 6.83 (d, $J=3$ Hz, 1H, H-3), 6.86 (d, $J=9$ Hz, 1H, H-6), 7.36–7.41 (m, 1H, Ph), 7.46–7.48 (m, 4H, Ph); ^{13}C-NMR ($CDCl_3$) δ 14.8 (Me), 65.2 (CH_2), 114.2 (CH, C-5 or C-6), 115.1 (C-5 or C-6), 117.6 (CH, C-3), 127.0 (Ph), 127.8 (Ph), 129.3 (Ph), 132.2 (C-2), 138.1 (Ph), 149.5 (C-1), 149.9 (C-4); LR-FABMS m/z (relative intensity) 214 (100), 186 (14); HRFABMS m/z 214,0996 (M^+) ($C_{14}H_{14}O_2$, -0.2 mmu)

4.9. 5,5′-Diethoxy-2,2′-dihydroxy-4,4′-diphenylbiphenyl (19)

Obtained in 40% yield, m.p. 194–195°C; ^{1}H-NMR ($CDCl_3$) δ 1.31 (t, $J=7$ Hz, 3H, Me), 3.97 (q, $J=7$ Hz, 2H, OCH_2), 5.75 (bs, 1H, OH), 6.94 (s, 1H, H-6), 7.04 (s, H-3), 7.34 (t, 1H, $J=7$ Hz, *p*-Ph), 7.41 (t, 2H, $J=7$ Hz, *m*-Ph), 7.59 (t, 2H, $J=7$ Hz, *o*-Ph); ^{13}C-NMR ($CDCl_3$) δ 14.8 (Me), 65.2 (CH_2), 116.1 (C-6), 119.2 (C-3), 123.5 (C-1), 127.1 (Ph), 127.9 (Ph and C-4), 129.3 (Ph), 132.5 (Ph), 146.6 (C-2), 151.1 (C-5); LRMS (12 eV) m/z (relative intensity) 426 (M^+, 100), 427 [$(M+H)^+$, 15]; HRFABMS m/z 426.1833 (M^+) ($C_{28}H_{26}O_4$, -0.2 mmu).

4.10. 5,5′-Diethoxy-2,2′-dihydroxy-4,4′-dichlorobiphenyl (20)

Obtained in 61% yield from 2-chlorobenzoquinone (**8**, 120 mg, 0.68 mmol); m.p. 170–171°C; IR (film) (ν_{max} 3401 (bs) cm^{-1}, ^{1}H-NMR ($CDCl_3$) δ 1.46 (t, 3H, $J=7$ Hz, CH_3), 4.04 (q, 2H, $J=7$ Hz, CH_2), 5.31 (s, 1H, OH), 6.79 (s, 1H, H-6), 7.08 (s, 1H, H-3); ^{13}C-NMR ($CDCl_3$) δ 14.7 (CH_3), 65.8 (CH_2), 116.3 (C-6), 118.8 (C-3), 122.6 (C-1), 124.3 (C-4), 146.5 (C-2), 149.2 (C-5); LRMS (12 eV) m/z (relative intensity) 342 (M^+, 100), 344 (65), 346 (6), 314 (10), 286 (37); HRFABMS m/z 342.0438 (M^+) ($C_{16}H_{16}O_4Cl_2$, -1.2 mmu).

4.11. 5,5′-Diethoxy-2,2′-dihydroxy-4,4′-dimethylbiphenyl (21)

Obtained in 79% yield from 2-methylbenzoquinone (**9**, 122 mg, 1 mmol); m.p. 168–169°C; IR (film)

(ν_{max} 3441 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.38 (t, $J = 7$ Hz, 3H, Me), 2.21 (s, Me), 3.96 (q, $J = 7$ Hz, 2H, OCH_2), 6.69 (s, H-6), 6.79 (s, H-3); ^{13}C-NMR ($CDCl_3$) δ 14.9 ($CH_2\underline{C}H_3$), 16.0 (Me), 64.4 (CH_2), 113.8 (C-6), 118.9 (C-3), 121.3 (C-1), 128.8 (C-4), 146.0 (C-2), 151.6 (C-5); HMQC 2.20/16.0, 3.95/64.4, 6.69/113.8, 6.79/118.9; HMBC ($^nJ_{CH} = 9$ Hz) 1.38 (Me)/64.4, 2.21 (Me)/151.6, 128.8, 118.9, 3.95 (CH_2)/151.6, 14.9, 6.69 (CH)/151.6, 145.9, 128.8, 121.3, 6.79 (CH)/151.6, 145.9, 121.3; LRMS (12 eV) m/z (relative intensity) 302 (M^+, 100); HRFABMS m/z 302.1510 (M^+) ($C_{18}H_{22}O_4$, 0.8 mmu).

4.12. 4,4′-Diethoxy-1,1′-dihydroxy-2,2′-binaphthyl (**23**)

Obtained in 35% yield from 1,4-naphthoquinone (158 mg, 1 mmol); m.p. 190–191°C; IR (film) (ν_{max} 3422 (bs) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.53 (t, $J = 7$ Hz, 3H, Me), 4.17 (bs, 2H, OCH_2), 5.39 (bs, 1H, OH), 6.72 (s, 1H, H-3), 7.59 (bs, 2H, H-5 and H-8), 8.29 (bs, 2H, H-6 and H-7); ^{13}C-NMR ($CDCl_3$) δ 14.8 (Me), 64.1 (CH_2), 106.1, 115.0, 122.0 (C–H), 122.2 (C–H), 125.9, 126.2 (C–H), 126.5 (2xC–H), 142.4 (C-1), 149.4 (C-4); LRMS (12 eV) m/z (relative intensity) 374 (M^+, 100), 328 (11), 299 (21), 216 (82), 186 (93), 172 (69); HR-FABMS m/z 374.1545 (M^+) ($C_{24}H_{22}O_4$, -2.7 mmu).

4.13. 4-Ethoxy-1-naphthol (**24**)

It was obtained in 9% yield; oil, IR (film) (ν_{max} 3411 (sb), 1625 (s), 1595 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.53 (t, 3H, $J = 7$ Hz, CH_3), 4.13 (q, 2H, $J = 7$ Hz, CH_2), 5.10 (bs, 1H, OH), 6.62 (d, $J = 8$ Hz, 1H, H-2), 6.70 (d, $J = 8$ Hz, 1H, H-3) 7.40–7.50 (m, 2H, H-6 and H-7), 8.10 (m, 1H, H-5 or H-8), 8.26 (m, 1H, H-5 or H-8).

4.14. 1,4-Diethoxynaphthalene (**25**)

Obtained in 3% yield; oil, IR (film) (ν_{max} 1595 (s), 1273 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.51 (t, 6H, $J = 7$ Hz, CH_3), 4.14 (q, 4H, $J = 7$ Hz, CH_2), 6.68 (s, 2H, H-2 and H-3), 7.47–7.50 (m, 2H, H-6 and H-7), 8.20–8.24 (m, 2H, H-5 and H-8); LRFABMS m/z (relative intensity) 216 (100), 187 (24), 174 (10), 159 (26).

4.15. 2-Ethyl-1,4-naphthoquinone (**26**)

Obtained in 4% yield; oil, IR (film) (ν_{max} 1663 (bs) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.23 (t, 3H, $J = 7$ Hz, CH_3), 2.61 (q, 2H, $J = 7$ Hz, CH_2), 6.78 (bs, 1H, H-3), 7.70–7.73 (m, 2H, H-6 and H-7), 8.05–8.11 (m, 2H, H-5 and H-8); LRFABMS m/z (relative intensity) 187 [$(M + 1)^+$, 17].

Acknowledgements

Fellowship from CAPES (Brazil) to V.F.F. is gratefully acknowledged. This work was supported in part by Department of Commerce, NOAA Sea Grant Project NA66RGO172.

References

[1] F.J. Schmitz, A. Park, Tetrahedron Lett. 34 (1993) 3983.
[2] F.J. Schmitz, F.S. DeGuzman, Y.-H. Choi, M.B. Hossain, S.K. Rizvi, D. van der Helm, Pure Appl. Chem. 62 (1990) 1393.
[3] F.J. Schmitz, Y.-H. Choi, A. Park, J. Nat. Prod. 56 (1993) 1431.
[4] F. Sainte, B. Serckx-Poncin, A.-M. Hesbain-Frisque, L.A. Ghosez, J. Am. Chem. Soc. 104 (1982) 1428.
[5] Z. Florjanczyk, W. Kuran, S. Pasynkiewicz, G. Kwas, J. Organomet. Chem. 112 (1976) 21.
[6] Z. Florjanczyk, W. Kuran, S. Pasynkiewicz, A. Krasnicka, J. Organomet. Chem. 145 (1978) 21.
[7] Z. Florjanczyk, E. Szymanska-Zachara, J. Organomet. Chem. 259 (1983) 127.
[8] M. Laus, M.C. Bignozzi, A.S. Angeloni, G. Calli, E. Chiellini, Macromolecules 26 (1993) 3999.
[9] G. Kumaran, G.H. Kulkarni, Indian J. Chem. 33B (1994) 168.
[10] J.J. Parlow, Tetrahedron Lett. 37 (1996) 5257.
[11] P.E. Baker, A Hudson, R.A. Jackson, J. Organomet. Chem. 208 (1981) C1.
[12] A. Hudson, J. Organomet. Chem. 194 (1980) 137.
[13] C. Blomberg, H.H. Grootveld, T.H. Gerner, F. Bickelhaupt, J. Organomet. Chem. 24 (1970) 549.
[14] H. Joela, S. Kasa, R. Mäkelä, E. Sato, K. Hannomen, Magn. Reson. Chem. 28 (1990) 261.
[15] T.L. Simándi, A. Rockenbauer, Ero. Polym. J. 27 (1991) 523.
[16] R.K. Norris, S. Sternhell, Aust. J. Chem. 26 (1973) 333.
[17] V.F. Ferreira, F.J. Schmitz, Org. Prep. Proced. Int. 30 (1998) 115.
[18] B. Wladislaw, L. Marzorati, C. Di Vita, Synthesis (1983) 464.