Mechanochemical Conversion of (5-5')-(β-O-4)
Type of Lignin Model Compound.*1

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Abstract: As a lignin model compound having a biphenyl structure, (5-5')-(β-O-4) type of Compound [I] was synthesized and treated mechanically to find out the reaction mechanisms. Mechanical treatments of Compound [I] with a CBM (ceramic ball mill) in air furnished four products, but those of VBM (vibration ball mill) in air or nitrogen afforded six products, respectively, as shown in Table 1 and Fig. 2. Among the products, the corresponding p-carbonyl phenol 1 was obtained in the highest yields. Differently from the cases of syringylglycerol-19-guaiacyl ether shown in the previous report, treatments of Compound [I] with both CBM and VBM resulted in much lower yields of the products. The reason for this was ascribed to the presence of a large hydrophobic trityl ether group bound to the sterically hindered biphenyl group via the methylene bridge.

1. Introduction

According to Hosoya and Nakano [1] and also to Omori and Dence [2], the treatment of a p-carbonyl phenol with alkaline H2O2 furnished relatively high amounts of the corresponding p-hydroquinone according to the Dakin-type of oxidation. Cole and Sarkanen [3] found the remarkable effect of thiol derivatives on both bleaching mechanical pulps and stabilizing their brightnesses. They suggested further that a p-benzoquinone derivative, as a plausible chromophore, can be reduced with thiol derivatives to the corresponding p-hydroquinone.

Lee and Sumimoto [4] reported that the treatment of veratrylglycerol-β-guaiacyl ether with a ceramic ball mill (CBM) gave almost no reaction product, but veratrylglycerol-β-vanillin ether furnished about 18.8% of vanillin, a p-carbonyl phenol, and others. When phenylcoumaran derivatives [5, 6] having an aldehyde group on its B-ring were treated with a CBM, a vibration ball mill (VBM) or a laboratory refiner, a few per cents of stilbenes having a p-carbonyl phenol structure on the B-ring were obtained. When the latter stilbene was treated with alkaline H2O2, the corresponding stilbene p-hydroquinone was produced. Under irradiation, the latter was easily oxidized to the corresponding p-benzoquinone, which could be reduced with thiol derivatives to the corresponding p-hydroquinone.

Wu and Sumimoto [7] recently reported their results dealing with the treatment of veratrylglycerol-β-syringaldehyde ether with a VBM under air or nitrogen in the presence of water. Replacement of the air in a VBM by nitrogen resulted in slightly increased yields of syringaldehyde, a p-carbonyl phenol, but the yields of p-benzoquinone decreased dramatically. Considering the whole reaction mechanisms, greatly plausible co-existence of •O2H, •OH, and •H radicals in the aqueous reaction media was proposed.

In a more recent paper [8], mechanical treatments of a-(2-methoxyphenoxy)-β -hydroxypropiosyringone proved further the significant role of •O2H, •OH, and •H radicals in the mechanical treatment. In the previous report [9], mechanical treatment of syringylglycerol-β-guaiacyl ether as a typical model compound of hardwood lignin was made with CBM, VBM, and a laboratory refiner. Whole reactions were shown to proceed by the similar radical reaction mechanisms. The facts mentioned above suggest that the ultrasonic waves generate in the aqueous media...
of mechanical pulping. Further confirmation of this assumption was made recently, and will be published elsewhere.

The present paper deals with the synthesis and the mechanochemical conversions of (5-5')-(β-O-4) type of Compound [I].

2. Experiment

2.1 Synthesis of (5-5')-(β-O-4) Type of Compound [I]

Synthesis of (5-5')-(β-O-4) type of Compound [I] from dehydrodivanillin (2) was conducted along the route shown in Fig. 1.

Identification of the products was made by a comparison of melting points (mp) and mixed mps with authentic samples, by the ultraviolet (UV) spectrum, and by direct inlet mass spectrum (DI-MS) as well as proton nuclear magnetic resonance (¹H-NMR) spectrum. DI-MS were recorded on a Shimadzu QP-1000 mass spectrometer. ¹H-NMR spectra were measured in CDCl₃ with Me₄Si as the internal standard.

2.1.1 Dehydrodivanillin (2)

To a solution of vanillin (5 g, 33 mmol) in 335 mL of hot water (70 °C), was added 167 mg of ferrous sulphate and 4.2 g (15 mmol) of potassium persulphate. Agitating the solution for 1 h gave a precipitate which was filtrated. The crude product was then dissolved in the minimum of 0.1 N sodium hydroxide. Acidification of the solution left a yellowish precipitate which was filtrated and washed with water giving the product of 3.1 g (62%). mp > 300 °C (mp 305 °C [10]); DI-MS (70 eV)m/z (%): 302(3.5, M⁺), 271(100), 225(3.1), 151(1.7) and 120(1.3).

Fig. 1 Synthetic pathway of (5-5')-(β-O-4) type of Compound [I].
2.1.2 Dehydrodivanillin Monomethyl Ether (3)

Sodium hydroxide (0.06 g, 0.1 mmol), dimethyl sulphate (0.2 mL, 2 mmol), and benzyltrimethyl ammonium bromide (11) (0.0356 g, 0.1 mmol) as a phase-transfer catalyst were added to a mixture of dehydrodivanillin (2) (0.3 g, 1 mmol) in 9 mL each of dichloromethane and water. This was agitated at room temperature for 3 h. The organic layer was then separated from the reaction mixture, and the aqueous layer was extracted twice with 10 mL portions of dichloromethane. The combined organic extracts were evaporated in vacuo and the residue was dissolved in 5 mL of ether. The mixture was extracted twice with 2 mL of 2 N aqueous ammonia solution, then with 2 mL of 2 N aqueous sodium hydroxide solution, and washed finally with brine. After drying over anhydrous sodium sulphate, the solvent was evaporated in vacuo. The residue of 0.13 g was recrystallized from benzene to give white powder (0.117 g, 39%) with mp 197 °C, (mp 196.5–197 °C (12)). DI-MS (70 eV) m/z (%): 316(2.5, M+), 285(100), 225(1.1), 151(1.3) and 120(3.1); 'H-NMR (400 MHz, CDCI3) δ (ppm): 3.8(3H, s, -OMe), 3.99(3H, s, -OMe), 4.03(3H, s, -OMe), 7.21–7.53(4H, m, aromatic protons), 9.86(2H, s, -CHO), 9.93(2H, s, -CHO).

2.1.3 Monoalcohol (4)

To a stirred solution containing 0.2 g (0.6 mmol) of dehydrodivanillin monomethyl ether (3) in 15 mL of dioxane, 0.023 g (0.6 mmol) of sodium borohydride in 1 mL of methanol was added dropwise over a period of 15 min at room temperature. The reaction mixture was extracted twice with 10 mL of ether. The ether layer was washed twice with 10 mL of 2 N aqueous HCI, finally with water. The solvent was dried with sodium sulphate and concentrated in vacuo yielding 0.15 g (75%) of monoalcohol (4) as a colorless syrup. DI-MS (70 eV) m/z(%): 318(39.2, M+), 285(21.0), 270(20.7), 269(100), 185(13.6), 115(34.3); 'H-NMR (400 MHz, CDCI3)(acetate) δ (ppm): 2.13(3H, s, -OAc), 2.16(3H, s, -OAc), 3.62(3H, s, -OAc), 3.98(3H, s, -OAc), 4.03(3H, s, -OAc), 5.12(2H, s, -CH2OAc), 6.91(2H, s, aromatic protons), 7.62(2H, s, aromatic protons), 9.98(1H, s, -CHO).

2.1.4 Trityl Ether (5)

A mixture of monoalcohol (4) 0.1 g (0.3 mmol), trityl chloride 0.092 g (0.6 mmol) of sodium borohydride in 1 mL of methanol was added dropwise over a period of 15 min at room temperature. The reaction mixture was extracted twice with 10 mL of ether. The ether layer was washed with 10 mL of 2 N aqueous ammonia solution, then with 2 mL of 2 N aqueous sodium hydroxide solution, and washed finally with brine. After drying over anhydrous sodium sulphate, the solvent was evaporated in vacuo. The residue of 0.13 g was recrystallized from benzene to give white powder (0.117 g, 39%) with mp 197 °C, (mp 196.5–197 °C (12)). DI-MS (70 eV) m/z(%): 316(2.5, M+), 285(100), 225(1.1), 151(1.3) and 120(3.1); 'H-NMR (400 MHz, CDCI3) δ (ppm): 3.8(3H, s, -OMe), 3.99(3H, s, -OMe), 4.03(3H, s, -OMe), 7.21–7.53(4H, m, aromatic protons), 9.86(2H, s, -CHO), 9.93(2H, s, -CHO).

2.1.5 Benzyl Ether (6)

To a solution of trityl ether (5)(0.05 g, 0.09 mmol) in 0.2 mL of N, N-dimethylformamide (DMF), powdered potassium carbonate (0.037 g, 0.1 mmol) and benzyl chloride (0.013 g, 0.1 mmol) were added and stirred at 100 °C for 3 h. The reaction mixture was put into ice water to give the yellow precipitates, which were recrystallized from ethanol/hexan to give 4.72 g(92.8%) of benzyl ether (6) having mp 60 – 65 °C ; DI-MS (70 eV) m/z(%): 650(22.2, M+), 269(17.9), 243(18.1), 165(58.6), 105(14.4), 91(100).

2.1.6 Condensation Product (9)

To the stirred solution of trityl ether (5)(0.05 g, 0.09 mmol) in 0.2 mL of N, N-dimethylformamide (DMF), powdered potassium carbonate (0.037 g, 0.1 mmol) and benzyl chloride (0.013 g, 0.1 mmol) were added and stirred at 100 °C for 3 h. The reaction mixture was put into ice water to give the yellow precipitates, which were recrystallized from ethanol/hexan to give 4.72 g(92.8%) of benzyl ether (6) having mp 60 – 65 °C ; DI-MS (70 eV) m/z(%): 650(22.2, M+), 269(17.9), 243(18.1), 165(58.6), 105(14.4), 91(100).
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2.1.7 Reduction Product (10)

To a stirred solution of anhydrous THF of 13 mL containing 0.0684 g of lithium aluminum hydride (LAH), 0.3381 g of condensation product (8) dissolved in 2.3 mL of anhydrous THF was added dropwise over a period of 1 h at 50 °C under nitrogen gas and the stirring was continued for additional 3 h. The reaction mixture was cooled at 0 °C and then 0.6 mL of water dissolved in 3 mL THF was added dropwise over a period for decomposition of excess LAH. The lithium complex was decomposed by adding dry ice, and the resulting inorganic lithium salt was filtered off and washed with ethyl acetate. The filtrate and the washings were combined and dried over sodium sulphate and the solvent was evaporated in vacuo. A colorless substance of 0.1911 g which gave one spot on the TLC plate developed with benzene:ethyl acetate:formic acid = 15 : 4 : 1 was obtained 0.1804 g of reduction product (10). DI-MS (70 eV) m/z (%) : 818 (2.7, M + ), 575 (8.1), 409 (2.8), 318 (15.9), 287 (3.8), 91 (100).

2.1.8 (5-5')-(0-4) Type of Compound [I]

To a mixed solution of compound (10)(0.6456 g) in 10.2 mL each of ethanol and dioxane, 0.045 g of palladium-charcoal was added. After stirring under hydrogen at room temperature for 3 h, palladium-charcoal was filtered off and the combined filtrates and washings were evaporated in vacuo to give a colorless oil of 0.4776 g. DI-MS (70 eV) m/z(%): 728 (1.2, M + ), 485 (5.3), 401 (1.8), 319 (14.1), 269 (100), 194 (17.5), 162 (15.4); 'H-NMR (400 MHz, CDCl3) (acetate), δ (ppm): 2.02 - 2.09 (6 H, m, -OAc), 2.38 (3H, s, aromatic -OAc), 3.64 (3H, s, -OMe), 4.00 (3H, s, -OMe), 4.04 (3H, s, -OMe), 4.08 (3H, s, -OMe), 4.63 (1H, m, β-H), 5.16 - 5.21 (4H, m, -CH3), 5.99 (1H, t, J = 5.1 Hz, a-H), 7.01 - 7.54 (23H, m, aromatic protons).

2.2 Mechanical Treatment of Compound [I]

Separation and determination of chemical structures for the mechanochemical conversion products (1 to 6) from Compound [I] were accomplished by preparative thin layer chromatography (TLC) and high-pressure liquid chromatography (HPLC). Preparative TLC was performed on a glass sheet with a silica-gel (Kieselgel 60 PF254) layer of 1.5 mm thickness. HPLC was performed on Jasco Trioretor-II using a Chempac pack column (20×270 mm). UV spectra were recorded on a Hitachi model 200-20 spectrophotometer using MeOH as a solvent.

2.2.1 Treatment of Compound [I] in Air with CBM and VBM.

One hundred mg of Compound [I] dissolved in 2 mL of dichloromethane was dispersed onto 0.1 g of filter paper pulp, and the solvent was removed in vacuo. One mL of water was added to both 0.1 g of pulps and treated by either CBM or VBM under air for 1h. Extraction of the reaction mixture in CBM of VBM was made successively three times with 100 mL portions of acetone-chloroform mixture (1 : 1), and filtered. The combined extracts were filtered, dried over anhydrous sodium sulphate, and evaporated in vacuo. The residues were 60.8 mg (CBM), 59.0 mg (VBM) respectively.

The starting materials [I] of 58.3 mg (CBM) or 50.5 mg (VBM) were recovered, respectively, from the reaction mixture by preparative TLC (benzene:ethyl acetate:formic acid = 15 : 4 : 1), and the resulting products were separated and purified further by HPLC. The yields of the identified compounds are shown in Table 1.

2.2.2 Treatment of Compound [I] in N2 with VBM

One hundred mg of Compound [I] was dispersed into 0.1 g of filter paper pulp, and the solvent was removed in vacuo. One mL of water was added to the resulting pulp in VBM, and the air in VBM was replaced three times with nitrogen in a Glove Box (Tokyo Air Engineering Inc.), and then treated by usual manner for 1 h. From the reaction mixture of 92.0 mg, 80.3 mg of Compound [I] was removed by preparative TLC, and the residue was separated by HPLC. Identification of the seven isolated compounds was performed by DI-MS and 'H-NMR spectroscopy.

2.3 Identification of Mechanochemical Conversion Products

The chemical structures for six conversion products (1, 2, 3, 4, 5, 6) were identified by the comparison of DI-MS, 'H-NMR, and UV spectra as shown in Fig. 2. The Table. 1 Yields of Mechanochemical Conversion Products from Compound [I] (weight %)

<table>
<thead>
<tr>
<th>Condition</th>
<th>Recovery yield</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Total [I]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBM (air)</td>
<td>89.3</td>
<td>65.7</td>
<td>1.3</td>
<td>0.2</td>
<td>0.1</td>
<td>tr.</td>
<td>tr.</td>
</tr>
<tr>
<td>VBM (air)</td>
<td>80.4</td>
<td>60.2</td>
<td>3.5</td>
<td>1.0</td>
<td>0.5</td>
<td>0.1</td>
<td>0.7</td>
</tr>
<tr>
<td>VBM (N2)</td>
<td>87.1</td>
<td>82.4</td>
<td>3.0</td>
<td>0.2</td>
<td>0.2</td>
<td>tr.</td>
<td>tr.</td>
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yields of conversion products were determined by preparative TLC followed by HPLC and are shown in Table 1.

\( p \)-Carbonyl phenol 1: DI-MS (70 eV) m/z(%) : 726(6.1, M\(^+\)), 483(5.8), 319(21.5), 269(100), 152(34.4); \(^1\)H-NMR (400 MHz, CDCl\(_3\))(acetate), \( \delta \) (ppm): 2.06(3H, s, -OAc), 2.36(3H, s, aromatic -OAc), 3.58(3H, s, -OMe), 3.66(3H, s, -OAc), 3.76(3H, s, -OMe), 3.87(3H, s, -OMe), 5.18-5.26(2H, m, -CH\(_2\)), 5.34(1H, t, \( J = 5.6 \) Hz, \( \beta \)H), 7.01-7.54(23H, m, aromatic protons).

(5-5')-\( p \)-benzoquinone 2: DI-MS (70 eV) m/z(%) : 546(19.3, M\(^+\)), 303(22.6), 243(100), 137(31.6), 80(26.8), 69(35.6). UV\(_{\text{max}}\) (\( \lambda \)nm) 260 nm (1.2\( \times \)10\(^4\)), 321(2.8\( \times \)10\(^3\)).

2-(2-Methoxyphenoxy)-3-hydroxypropionic acid 3: mp 81-83 °C; DI-MS(70 eV) m/z(%) : 212(22.5, M\(^+\)), 182(100), 165(6.8), 137(12.8); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) : 3.79(3H, s, -OMe), 3.96(2H, d, \( J = 1.7 \) Hz, CHO), 4.59(1H, m, CH), 6.91(4H, m, aromatic protons).

Compound 4: DI-MS (70 eV) m/z(%) : 576(3.8, M\(^+\)), 333(19.3), 269(11.8), 243(100); \(^1\)H-NMR(400 MHz, CDCl\(_3\))(acetate), \( \delta \) (ppm) : 2.36-2.48(6H, m, -OAc), 3.80(3H, s, -OAc), 3.99(3H, s, -OMe), 4.03(3H, s, -OMe), 5.16(2H, m, -CH\(_2\)), 7.19 - 7.50(19H, m, aromatic protons).

(2-Methoxyphenoxy)-1,2-dihydroxy ethane 5: DI-MS (70 eV) m/z(%) : mp 130-132 °C ; 268(10.5, M\(^+\)), 225(11.8), 182(100), 166(7.1); \(^1\)H-NMR (400MHz, CDCl\(_3\))(acetate), \( \delta \) (ppm) : 2.41(6H, s, -OAc), 3.62(3H, s, -OMe), 4.10(2H, t, \( J = 1.1 \) Hz, -CH\(_2\)), 4.96(H, m, -CH), 6.87 - 7.64(4H, m, aromatic protons).

Compound 6: DI-MS (70 eV) m/z(%) : 696(20.5, M\(^+\)), 453(13.8), 269(10.5), 243(100); \(^1\)H-NMR (400 MHz, CDCl\(_3\))(acetate), \( \delta \) (ppm) : 2.38(3H, s, aromatic -OAc), 3.62(3H, s, -OAc), 3.81(3H, s, -OMe), 4.13(3H, s, -OMe), 4.31(3H, s, -OMe), 4.40 - 5.08(4H, m, -CH\(_2\)) 6.78 - 7.64(23H, m, aromatic protons).

3. Results and Discussion

3.1 Synthesis of (5-5')-(\( \beta \)-O-4) Type of Compound [I]

Dehydrodivanillin (2) was synthesized by the method of Castellan and others [13] in the yield of 62%. Monomethylation of dehydrodivanillin (2) by the method of Mikawa and Sato [12] furnished monomethyl ether (3) in only 15% yield. Therefore, benzyltri-n-butylammoniumbromide [11] was utilized as a phase-transfer catalyst (PTC) to give the increased yield of monomethyl ether (3) up to 37%. Reduction of dehydrodivanillin monomethyl ether (3) with sodium borohydride furnished monoalcohol (4) in about 75% yield. After preparation of trityl ether (5) from monoalcohol (4) in about 54.3% yield, benzyl ether (6) of the trityl ether (5) was pre-
pared in about 92.8% yield. According to the method of Nakatsubo and others (14), condensation reaction of compound (6) with ethyl 2-methoxyphenoxy acetate (7) yielded the condensation product (8), which was reduced with lithium aluminum hydride to give compound (9). The latter was reduced by palladium/charcoal to give the final Compound (11). The yields of condensation product (8) in 53% was considerably low in comparison with the case of syringylglycerol-β-guaiacyl ether. Furthermore, because of having both the highly steric hindrance and the large hydrophobicity due to co-occurrence of a biphenyl and a trityl ether group, the overall yields were only in 2.7% from vanillin.

3.2 Mechanical Treatments of (5-5')-(β-O-4) Type of Compound (11) with CBM, and VBM

Results given by the mechanical treatment of (5-5')-(β-O-4) type of Compound (11) are shown in Table 1 and Fig. 2-4. Treatment of Compound (11) with both CBM, and VBM furnished p-carbonyl phenol phenol 1 in the highest yields, respectively. Among them, treatment of Compound (11) with CBM under the presence of air and 1.0 mL of water afforded only four products, 1, 2, 3, and 6 in the yields of 1.3, 0.2, 0.1%, and trace, respectively. However, the mechanical treatments with either VBM in the air (VBM-air) or VBM in nitrogen (VBM-N₂) under the presence of 1.0 mL of water furnished two additional products, 4, and 5 as shown in Table 1. Unfortunately, however, treatment of Compound (11) with a laboratory refiner could not be made because of the shortage of materials of Compound (11).

As shown in Table 1 and Fig.2, treatments of Compound (11) with CBM-air, VBM-air and VBM-N₂ in the presence of water, respectively, furnished the corresponding p-carbonyl phenol 1 in the yields of 1.3, 3.5 and 3.0%, respectively. As shown in Fig. 3, the reaction proceeds by simultaneous abstraction of two •H radicals, namely one from phenolic OH and another one from CαH, respectively, to give the p-carbonyl phenol 1 in the highest yields. Differently from the case of syringylglycerol-β-guaiacyl ether in the previous report (8), treatments of a biphenyl type of Compound (11) with both CBM and VBM resulted in much lower yields of the corresponding products. As mentioned above, Compound (11) contains an extremely large trityl ether group, therefore having both strong steric hindrance and high hydrophobicity as shown in Fig.4. Therefore, approach of water molecules carrying •O₂H, •OH, and •H radicals to the reaction sites is effectively prevented from valid collision as shown in Fig.4. This is almost the sole reason for such low yields of mechanochemical conversion products from Compound (11) as shown in Table 1.

As mentioned in the previous paper (9), mechanical treatment of a para-carbinol phenol e.g. Compound (11) affords the corresponding p-carbonyl phenol 1' which is followed by Dakin-type radical reaction due to •O₂H and •H radicals as shown in Fig.3. Now the splitting reactions between Car-Cα and Cα-Cβ bonds take place by the work of •O₂H, •OH, and •H radicals to give a pair of products, (5-5')-p-benzoquinone 2 and α-(2-methoxy-...
phenoxyl-β-hydroxypropionic acid 3. Another pair, a biphenyl type of carboxylic acid 4 and (2-methoxyphenoxy)-1,2-dihydroxy ethane 5 were also provided as shown in Fig.2 and 3. Finally, compound 6 is provided by exclusion of HCHO.

When Compound [I] was treated with either VBM in the air or nitrogen, 3.5 and 3.0% of compound 1 were obtained in the highest yields. This proved the significant function of •OH radicals to produce a p-carbonyl phenol as shown in Fig.3. The yields of 5-substituted-p-benzoquinone 2 under air or nitrogen proved to be 1.0 or 0.2% yields, respectively. The large differences between the two are almost similar to the results in the previous paper [8]. The big differences are therefore ascribed to the difference in gaseous constituents, in spite of the relatively smaller differences in compound 3. Another pair of compounds 4 and 5 was given in 0.1 and 0.1% yields, respectively. The last compound 6 was given under air in 0.7% yield, but under nitrogen in 0.1% yield. Therefore, it is highly probable that high concentration of •O2H, •OH, and •H radicals are kept at a certain level only under air. Based on the facts mentioned above, Dakin-type of radical oxidation reaction of Compound [I] may initiate with the attack by •O2H, •OH, and •H radicals as shown in Fig.3.

4. Conclusion

Treatment of biphenyl type of Compound [I] with CBM-air, VBM-air, and VBM-N2 furnished 1.3, 3.2 and 3.0% of the corresponding p-carbonyl phenol 1 in the highest yields, respectively. These are followed by a complex Dakin-type of radical oxidation with attack by •O2H and •H radicals to the α-carbonyl groups yielding compounds 2 and 3 on the one hand, and compounds 4 and 5 on the other hand. Differently from the case of syringylglycerol-β-guaiacyl ether, mechanochemical conversion products from biphenyl type of Compound [I] with CBM-air, VBM-air, and VBM-N2 treatments, were obtained in much lower yields. This was ascribed to the strong steric hindrance due to a biphenyl type of structure on the one hand, and also to the presence of a large hydrophobic trityl ether group on the other hand.

References