Montmorillonite clay catalysis. Part 14.[1] A facile synthesis of 2-substituted and 2,2-disubstituted 1,3-benzodioxoles

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Received (in Cambridge) 14th July 1998, Accepted 9th September 1998

A series of 2-substituted and 2,2-disubstituted 1,3-benzodioxoles have been synthesised by reaction of catechol and pyrogallol with corresponding aldehydes and ketones catalysed by montmorillonite KSF or K-10. The reactions are completed within 2.7–24 h to give satisfactory yields. Ketones give better yields than aldehydes, although highly sterically hindered ketones and diaryl ketones fail to react at all.

Introduction

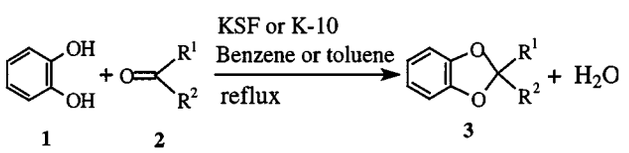
The 1,3-benzodioxole ring system is an integral part of many natural products, such as sesamol and piperine.[2–5] Recently, 1,3-benzodioxoles with various substituents at the 2-position have received more and more attention. 1,3-Benzodioxole derivatives are inhibitors of mono-oxygenase enzymes,[6] and have been widely used in pesticides or pesticide intermediates,[7–10] herbicides,[11] antioxidants,[12–13] antimicrobials[14] and medicines.[15,16] The synthesis of 1,3-benzodioxole derivatives is also useful for the protection of catechols[17–20] or carbonyl compounds[21] in organic synthesis and thus their synthesis assumes great importance in biological chemistry and organic synthesis. The acetal ring is stable to HNO_3,[6] $Pb(OAc)_4$[2] and BuLi[18,22] for example while the cleavage of 1,3-benzodioxoles has been reported by several reagents, such as NaI–AcCl,[23] boron tribromide,[24] and $NaN(SiMe_3)_2$ or Li(*i*-Pr).[25]

1,3-Benzodioxoles can be synthesised from catechols and *gem*-dihalides.[12*a*,26–27] However, there are few *gem*-dihalides commercially available and they are usually expensive. Transacetalisation of ketone dimethyl acetals with catechol has also been developed in the presence of boron tribromide.[24] Another obvious synthetic route is the condensation of catechols with carbonyl compounds with acid catalysts such as phosphorus pentoxide.[28,29] In this procedure, a large amount of phosphorus pentoxide is used as both acid catalyst and dehydrating agent and the work-up is tedious and inconvenient. Toluene-*p*-sulfonic acid is widely employed in this reaction,[6,12*c*,30,31] and if the water formed is removed by azeotropic distillation, only catalytic amounts of toluene-*p*-sulfonic acid are needed. However, the disadvantage of this method is the long reaction time (8–120 h, ref. 6) and unsatisfactory yield. In recent years, other catalysts, such as trimethylsilyl chloride (TMSCl)[32] and phosphorus trichloride[33] have also been used to catalyse the condensation of catechol with carbonyl compounds.

Solid acids have been recently used as efficient catalysts for a variety of organic reactions.[34,35] We have developed an efficient and convenient preparation of acetals catalysed by montmorillonite clay.[36] This prompted us to use montmorillonite clays to catalyse the synthesis of 2-substituted and 2,2-disubstituted 1,3-benzodioxoles from catechol and the corresponding aldehydes and ketones. We report here a facile synthesis of substituted 1,3-benzodioxoles from catechol and pyrogallol with carbonyl compounds catalysed by montmorillonite KSF or K-10.

Results and discussion

As shown in Table 1, in the presence of montmorillonite KSF, a series of 2,2-disubstituted 1,3-benzodioxoles were prepared from catechol **1** and ketones **2** in benzene or toluene with azeotropic distillation (Scheme 1). The reactions were completed within 2.7–24 h to give satisfactory yields in most cases. The crude products **3** could be easily obtained by filtration of the catalyst followed by evaporation of the solvent. The present procedure gives reproducibly high yields but needs much shorter reaction times than with toluene-*p*-sulfonic acid catalyst.[6] For example, with toluene-*p*-sulfonic acid catalyst and heating for 72, 24 and 120 h, **3b**, **3l** and **3s** were obtained in 83, 90 and 76% yield respectively.[6] However, our procedure with KSF catalyst and heating for 7, 2.7 and 24 h gave **3b**, **3l** and **3s** in 94, 93 and 73% respectively.



Scheme 1

The structure of ketones **2** have a strong influence on the reaction. As shown in Table 1, acyclic aliphatic ketones (entries **2a–2f**) gave good to excellent yields of the corresponding 2,3-disubstituted 1,3-benzodioxoles **3a–2f**, while β-keto ester **2h** gave a very poor yield (9%) of the corresponding product **3h**, (this may be due to facile tautomerisation to the enol form, thus reducing the electrophilicity of the carbonyl group). The degree of steric hindrance in ketones **2** had a large effect on the reaction. Dibenzyl ketone **2i** provided only 30% yield of 2,2-dibenzyl-1,3-benzodioxole **3i**, whereas 2,4-dimethylpentan-3-one **2j**, 4,4-dimethylcholest-5-en-3-one **2p**, benzophenone **2w** and anthrone **2x** could not provide the corresponding 1,3-benzodioxoles. α,β-Unsaturated ketones show very little tendency to undergo this reaction, for example, 4-phenylbut-3-en-2-one **2u** gave **3u** only in 9% yield with KSF and 18% yield with K-10, while others such as cholest-4-en-3-one **2q** and cholest-4-ene-3,6-dione **2r** failed to react at all.

Five and six-membered ring ketones gave excellent yields of products. For example, cyclohexanone **2l** gave 93% of spiro-[1,3-benzodioxole-2,1′-cyclohexane] **3l**, and 5α-cholestan-3-one **2m** provided **3m** in 99% yield. However, cyclooctanone **2o** provided only 24% of spiro[1,3-benzodioxole-2,1′-cyclooctane] **3o**, and only 56% with K-10; this might relate to its ring tension.

Hexane-2,5-dione **2g**, when the molar ratio of **2g**:**1** was 3.7, gave 2-methyl-2-(3-oxobutyl)-1,3-benzodioxole **3g** (57%) as the major product with only 2.3% of 2,2′-dimethyl-2,2′-ethylene-bis(1,3-benzodioxole) **3ga** (Scheme 2). This illustrates that 1,4-dicarbonyl compounds could be selectively protected as mono-

Table 1 Preparation of 2,2-disubstituted 1,3-benzodioxoles catalysed by KSF

Ketone **2**	Catalyst/solvent/*t* (h)	Ratio[a]	Product	Yield (%)[b]	Bp(Torr) or Mp/°C Found	Reported
2a Acetone	KSF/benzene/10	1:10	**3a**	70	80–82(30)	50–51(2.5)[c]
2b Butanone	KSF/benzene/7	1:7.3	**3b**	94	95–97(30)	64–65(2.5)[c]
2c Hexan-2-one	KSF/toluene/12	2:1	**3c**	80[d]	125–127(30)	84–86(1.5)[c]
	K-10/toluene/6	2:1	**3c**	91[d]		
2d Methyl isobutyl ketone	KSF/benzene/7	1:2.8	**3d**	83	126–129(32)	96–97(5)[c]
2e Heptan-2-one	KSF/toluene/12	1:2	**3e**	97	146–147(35)	114–116(4.5)[c]
2f Octan-2-one	KSF/toluene/9	1:2	**3f**	92	156–159(32)	100–101(1)[c]
2g Hexane-2,5-dione	KSF/toluene/11	1:3.7	**3g**	57[e]	—	
			3ga	2.3[f]	120–121	
2h Ethyl acetoacetate	KSF/toluene/11.5	1:2	**3h**	9	—	130–132(5)[c]
2i Dibenzyl ketone	KSF/toluene/12	1:2.1	**3i**	30	—	
2j 2,4-Dimethylpentan-3-one	KSF/toluene/9	1:2		no reaction		
2k Cyclopentanone	KSF/toluene/3	1:1	**3k**	71	147–150(35)	114–115(4.5)[c]
2l Cyclohexanone	KSF/benzene/2.7	1:3.3	**3l**	93	49–49.5	45–48[c]
2m 5α-Cholestan-3-one	KSF/benzene/3	2.9:1	**3m**	99[d]	155–156	—
2n Cycloheptanone	KSF/toluene/12	1:2	**3n**	64	57–59	55–57[c]
2o Cyclooctanone	KSF/toluene/12	1:2	**3o**	24	68–70	—
	K-10/toluene/7	1:2	**3o**	56	68–70	
2p 4,4-Dimethylcholest-5-en-3-one	KSF/toluene/7	2:1		no reaction		
2q Cholest-4-en-3-one	KSF/toluene/8	2:1		no reaction		
2r Cholest-4-ene-3,6-dione	KSF/toluene/6	2:1		no reaction		
2s Acetophenone	KSF/toluene/24	1:2.1	**3s**	73		
2t *p*-Methoxyacetophenone	KSF/toluene/15	1:2	**3t**	67	67–68	—
	K-10/toluene/6	1:2	**3t**	94	67–68	—
2u 4-Phenylbut-3-en-2-one	KSF/toluene/12	1:2	**3u**	9	—	
	K-10/toluene/10	1:2	**3u**	18	—	
2v 2-Chloroacetophenone	KSF/toluene/13	1:2.5	**3v**	64	49–50	—
2w Benzophenone	KSF/xylenes/10	2:1		no reaction		
2x Anthrone	KSF/xylenes/10	2:1		no reaction		

[a] Catechol : ketone (mol : mol). [b] Isolated yield based on catechol. [c] Ref. 6. [d] Isolated yield based on ketone. [e] The product is 2-methyl-2-(3-oxobutyl)-1,3-benzodioxole **3g**. [f] The product is 2,2′-dimethyl-2,2′-ethylenebis(1,3-benzodioxole) **3ga**.

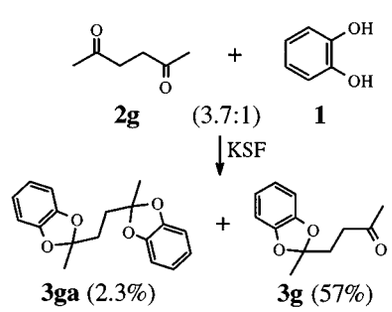
Table 2 Formation of 2-substituted 1,3-benzodioxoles catalysed by montmorillonites

Aldehyde **4**	Catalyst/solvent/*t* (h)	Ratio[a]	Product	Yield (%)[b]	Bp(Torr) or Mp/°C Found	Reported
n-Butyraldehyde **4a**	KSF/toluene/12	2.4:1	**5a**	44[c]	110–112(30)	75–80(3.5)[d]
	K-10/benzene/7	1:4	**5a**	62	110–112(30)	75–80(3.5)[d]
n-Heptaldehyde **4b**	KSF/toluene/12	2:1	**5b**	28[c]	—	
Cinnamaldehyde **4c**	KSF/toluene/9	1:2	**5c**	41	60–61	—
Benzaldehyde **4d**	KSF/toluene/8.5	1:3.1	**5d**	65	50–51	54–56[d]
p-Tolualdehyde **4e**	KSF/benzene/15	1:2.7	**5e**	67	57–58	148–150(2.5)[d]
	K-10/benzene/6	1:2.7	**5e**	70	57–58	—
3-Nitrobenzaldehyde **4f**	KSF/benzene/11	2.9:1	**5f**	38[c]	88–89	—

[a] Catechol : aldehyde (mol : mol). [b] Isolated yield based on catechol. [c] Isolated yield based on aldehyde. [d] Ref. 6.

benzodioxoles in the presence of KSF by using on excess of ketone.

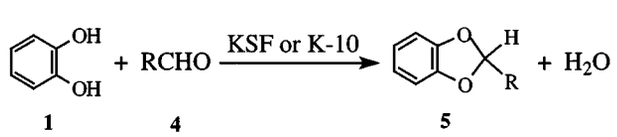
K-10 worked better than KSF for acetalisation of ketones in terms of reaction time and yield (Table 1, entries **2c**, **2o**, **2t** and **2u**). This may be due to the structure of K-10 which retains more acidic sites after treatment with mild acid, hence giving higher activity than the more strongly acid activated KSF.



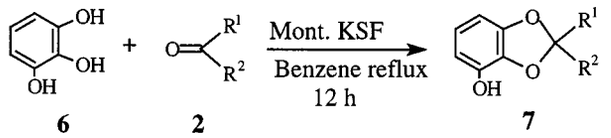
Scheme 2

We have also investigated the condensation of aldehydes **4** with catechol **1** under catalysis of KSF or K-10 (Scheme 3). The results are shown in Table 2. In contrast with ketone compounds, aldehydes gave an intractable mixture of complex by-products in this reaction and the acetals were obtained in only moderate yields (28–70%). This might be due to the aldehyde group being too reactive in the competing aldol reaction to give, for aliphatic aldehydes, cyclic trimerisation, oxidation and polymerisation as side reactions.

Pyrogallol **6**, shows higher reactivity than catechol **1** for this reaction. When **2e** and **2l** were treated with **6** under montmorillonite KSF catalysis, 2-methyl-2-pentyl-4-hydroxy-1,3-benzodioxole **7e** and 4-hydroxyspiro[1,3-benzodioxole-2,1′-cyclo-



Scheme 3



Scheme 4

Table 3 Synthesis of 2,2-disubstituted 4-hydroxy-1,3-benzodioxoles catalysed by KSF

Entry	R^1	R^2	Solvent	Pyrogallol : substrate	*t*/h	Product (Yield %)
2e	Me	Pentyl	Benzene	1 : 2	12	**7e** (99)
2l	-$(CH_2)_5$-		Benzene	1 : 2	12	**7l** (99)

hexane] **7l** were obtained in quantitative yield (99%) (Scheme 4, Table 3).

The montmorillonite catalysts can be reused several times without any significant decrease in activity after being washed with ethanol and activated at 120 °C.

Conclusions

In summary, we have developed an alternative method for the preparation of a variety of 2-substituted and 2,2-disubstituted 1,3-benzodioxoles catalysed by montmorillonite KSF and K-10. Aldehydes give moderate yields while ketones give good to excellent yields. Dicarbonyl compounds can selectively provide mono-benzodioxole compounds by using an excess of the ketone. Highly sterically hindered ketones, diaryl ketones and α,β-unsaturated ketones fail to react in this reaction. Pyrogallol shows a higher reactivity than catechol. Compared with the reported method,[6] our procedure needs much shorter reaction times and gives higher yields for most ketones. The present method has the additional advantages of mild conditions, easy set-up and work-up and non-corrosive, inexpensive, reusable and environmentally friendly catalysts.

Experimental

Boiling and melting points are uncorrected. Infrared (IR) spectra were recorded on Perkin-Elmer 983G, BTO-RAD and FTS-40 spectrometers (film). ^{1}H NMR spectra were measured on Bruker AC-80, Varian VXR-300 and INOVA-500 spectrometers, using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference. Mass spectra were obtained on a VG-7070E spectrometer, EI, 70 eV.

Montmorillonite KSF and K-10 were purchased from Aldrich and activated at 120 °C for 3 h prior to use. The ratio of montmorillonite KSF (or K-10) : catechol was 1 : 1 (w/w). Carbonyl compounds (**2** and **4**) and catechol (**1**) and pyrogallol (**6**) are commercially available. Aldehydes **4** were freshly distilled or recrystallised prior to use. All reactions were carried out under anhydrous conditions with removal of water by azeotropic distillation. For the cases of low-boiling point ketones, such as acetone or butanone, molecular sieves (3 Å) were employed for removal of water.

General procedure

The montmorillonite KSF (or K-10) catalyst (110 mg) was added to a solution of catechol **1** (110 mg, 1.00 mmol) or pyrogallol **6** (126 mg, 1.00 mmol) and ketone **2** (or aldehyde **4**) in benzene or toluene as indicated in Tables 1–3. The mixture was stirred at refluxing temperature for the length of time as shown in Tables 1–3 and the water was separated from the reaction system by azeotropic distillation with a water separator. The progress of the reaction was monitored by TLC (GF_{254}). After cooling, the catalyst was removed by filtration through a bed of silica gel, and washed with diethyl ether. After evaporation of the solvent, the crude products were chromatographed on silica gel (200–300 mesh), eluted with petroleum ether (bp 60–90 °C) and diethyl ether.

2-Methyl-2-hexyl-1,3-benzodioxole 3f. δ_H (80 MHz) 0.87 (3H, t, *J* 5.6, 6′-H), 1.20–1.50 (8H, m, 2′,3′,4′,5′-CH_2), 1.60 (3H, s, 2-CH_3), 1.88 (2H, t, *J* 3.1, 1′-CH_2) and 6.74 (4H, s, Ar-H); *m*/*z* 220 (M^+, 19%), 205 (7), 163 (2), 135 (100), 121 (2), 110 (13) and 81 (2).

2-Methyl-2-(3-oxobutyl)-1,3-benzodioxole 3g. Colorless oil; ν_{max}/cm^{-1} 3050, 2984, 1714, 1487, 1380, 1240, 1128, 950, 844 and 741; δ_H (300 MHz) 1.62 (3H, s, 2-Me), 2.12 (3H, s, 4′-H_3), 2.26 (2H, t, *J* 7.8, 1′-H), 2.61 (2H, t, *J* 7.8, 2′-H) and 6.73–6.81 (4H, m, 4,5,6,7-H_4); *m*/*z* 206 (M^+, 30%), 191 (5), 163 (14), 145 (4), 135 (100), 121 (6), 110 (15), 97 (22) and 81 (4).

2,2′-Dimethyl-2,2′-ethylenebis(1,3-benzodioxole) 3ga. Mp 120–121 °C, colorless needles from acetone; ν_{max}/cm^{-1} 3063, 2929, 1485, 1379, 1316, 1238, 1121, 1038, 870 and 741; δ_H (300 MHz) 1.61 (6H, s, 2,2′-di-Me), 2.13 (4H, s, 2 × CH_2) and 6.71–6.79 (8H, m, Ar-H); *m*/*z* 298 (M^+, 22%), 283 (1), 189 (4), 174 (4), 147 (2), 135 (100) and 110 (3).

2-Methyl-2-ethoxycarbonylmethyl-1,3-benzodioxole 3h. Colorless oil; δ_H (80 MHz) 1.20 (3H, t, *J* 7.1, -OCH_2CH_3), 1.99 (3H, s, 2-Me), 2.94 (2H, s, 1′-CH_2), 4.14 (2H, q, *J* 7.1, -OCH_2CH_3) and 6.78 (4H, s, Ar-H_4); *m*/*z* 222 (M^+, 19%), 176 (6), 149 (69), 135 (100), 121 (7) and 110 (22).

2,2-Dibenzyl-1,3-benzodioxole 3i. Colorless oil; ν_{max}/cm^{-1} 3063, 3031, 2923, 1602, 1485, 1239, 1099, 847, 737 and 699; δ_H (300 MHz) 3.17 (4H, s, 1′,1″-di-CH_2), 6.66 (4H, s, 4,5,6,7-H_4) and 7.18–7.295 (10H, m, Ph-H_{10}); *m*/*z* 302 (M^+, 19%), 245 (2), 211 (100), 157 (2), 135 (9) and 115 (4).

Spiro[1,3-benzodioxole-2,1′-cyclohexane] 3l. Mp 49–49.5 °C, colorless platelets from diethyl ether (lit.,[6] 45–48 °C).

Spiro[1,3-benzodioxole-2,3′-cholestane] 3m. Mp 155–156 °C, colorless needles from petroleum ether–ethyl acetate; ν_{max}/cm^{-1} 3055, 2925, 2860, 1485, 1360, 1240, 1172, 1050 and 730; δ_H (80 MHz) 0.67 (3H, s, 18′-H_3), 0.87 (3H, s, 19′-H_3), 0.87 (6H, d, *J* 5.9, 26′, 27′-H_6), 0.92 (3H, d, *J* 6.0, 21-H) and 6.74 (4H, s, Ar-H_4); *m*/*z* 478 (M^+, 100%), 462 (2), 369 (6), 215 (6), 162 (24), 147 (91), 134 (24), 121 (15) and 107 (28).

Spiro[1,3-benzodioxole-2,1′-cycloheptane] 3n. Colorless oil; δ_H (80 MHz) 0.88–2.20 (12H, m, 6 × CH_2) and 6.73 (4H, s, Ar-H_4); *m*/*z* 204 (M^+, 46%), 189 (5), 175 (7), 161 (28), 147 (100), 134 (15), 125 (57), 121 (14), 120 (22) and 110 (35).

Spiro[1,3-benzodioxole-2,1′-cyclooctane] 3o. Mp 68–70 °C, colorless needles from diethyl ether; δ_H (80 MHz) 0.88–2.16 (14H, m, 7 × CH_2) and 6.73 (4H, s, Ar-H_4); *m*/*z* 218 (M^+, 63%), 203 (2), 189 (14), 175 (14), 161 (11), 147 (100), 134 (56), 121 (11), 110 (56) and 109 (65).

2-Methyl-2-(*p*-methoxyphenyl)-1,3-benzodioxole 3t. Mp 67–68 °C, colorless platelets from acetone; ν_{max}/cm^{-1} 2992, 2938, 1612, 1485, 1380, 1238, 1177, 1130, 1085, 954, 836 and 743; δ_H (300 MHz) 1.97 (3H, s, 2-Me), 3.80 (3H, s, 4′-OMe), 6.79 (4H, s, 4,5,6,7-H_4), 6.89 (2H, d, *J* 8.6, 3′,5′-H_2) and 7.52 (2H, d, *J* 8.6, 2′, 6′-H_2); *m*/*z* 242 (M^+, 15%), 227 (17), 184 (1), 150 (1), 133 (100) and 118 (3).

2-Methyl-2-(2-phenylvinyl)-1,3-benzodioxole 3u. Colorless oil; ν_{max}/cm^{-1} 3065, 1660, 1603, 1485, 1364, 1237, 1195, 1100, 970, 823, 745 and 692; δ_H (300 MHz) 1.86 (3H, s, 2-Me), 6.33 (1H,

d, *J* 15.9, 1′-H), 6.80 (4H, s, 4,5,6,7-H_4), 6.87 (1H, d, *J* 15.9, 2′-H) and 7.22–7.40 (5H, m, Ph-H_5); *m*/*z* 238 (M^+, 100%), 222 (55), 128 (9) and 63 (9).

2-Chloromethyl-2-phenyl-1,3-benzodioxole 3v. Mp 49–50 °C, colorless needles from chloroform; ν_{max}/cm^{-1} 3065, 2960, 1485, 1236, 737 and 698; δ_H (300 MHz) 4.00 (2H, s, 2-CH_2Cl), 6.81–6.89 (4H, m, 4,5,6,7-H_4) and 7.40–7.645 (5H, m, Ph-H_5); *m*/*z* 246 (M^+, 13%), 210 (1), 197 (100), 181 (1), 169 (1), 137 (4) and 105 (19).

2-(2′-Phenylvinyl)-1,3-benzodioxole 5c. Mp 60–61 °C, colorless platelets from diethyl ether; ν_{max}/cm^{-1} 3066, 3030, 2930, 1658, 1482, 1356, 1234, 1145, 917 and 734; δ_H (300 MHz) 6.37 (1H, dd, *J* 16.2, 6.6, 1′-H), 6.60 (1H, d, *J* 6.6, 2-H), 6.83 (4H, s, 4,5,6,7-H_4), 6.92 (1H, d, *J* 16.2, 2′-H) and 7.31–7.47 (5H, m, Ph-H_5); *m*/*z* 224 (M^+, 100%), 197 (2), 181 (1), 165 (2), 147 (13), 131 (8), 121 (12), 115 (100) and 103 (11).

2-Phenyl-1,3-benzodioxole 5d. Mp 50–51 °C, colorless needles from diethyl ether (lit.,[6] 54–56 °C).

2-(*p*-Methylphenyl)-1,3-benzodioxole 5e. Mp 57–58 °C, colorless needles from diethyl ether (lit.,[6] bp 148–150 °C/2.5 mm Hg).

2-(*m*-Nitrophenyl)-1,3-benzodioxole 5f. Mp 88–89 °C, light yellow needles from diethyl ether; ν_{max}/cm^{-1} 3060, 2981, 1536, 1484, 1351, 1234, 1095, 948, 843 and 741; δ_H (300 MHz) 6.90 (4H, s, 4,5,6,7-H), 7.045 (1H, s, 2-H), 7.64 (1H, t, *J* 7.7, 5′-H), 7.93 (1H, d, *J* 7.7, 6′-H), 8.31 (1H, ddd, *J* 7.7, 2.4, 1.1, 4′-H) and 8.46 (1H, t, *J* 2.1, 2′-H); *m*/*z* 243 (M^+, 61%), 224 (5), 197 (11), 168 (1), 150 (5), 139 (4), 121 (100), 115 (14) and 104 (6).

2-Methyl-2-pentyl-4-hydroxy-1,3-benzodioxole 7e. Light yellow oil; ν_{max}/cm^{-1} 3262, 3060, 3030, 2954, 2869, 1643, 1504, 1478, 1389, 1315, 1255, 1058, 1026, 759 and 710; δ_H (500 MHz) 0.88 (3H, t, *J* 7.3, 5′-H_3), 1.29–1.32 (4H, m, 3′,4′-H_4), 1.47–1.50 (2H, m, 2′-H_2), 1.63 (3H, s, 2-Me), 1.91–1.94 (2H, m, 1′-H_2), 4.79 (1H, br s, 4-OH), 6.39 (1H, dd, *J* 7.8, 1.0, 5-H), 6.44 (1H, dd, *J* 7.8, 1.0, 7-H) and 6.66 (1H, t, *J* 7.8, 6-H); *m*/*z* 222 (M^+, 100%), 207 (17), 179 (15), 151 (100), 137 (9), 126 (100) and 108 (5).

4-Hydroxyspiro[1,3-benzodioxole-2,1′-cyclohexane] 7l. Mp 84–85 °C, light yellow blocks from diethyl ether (lit.,[37] mp 115–116 °C); δ_H (500 MHz) 1.48–1.51 (2H, m, 3′-H_2), 1.73 (4H, quintet, *J* 6.0, 2′, 4′-H_4), 1.92 (4H, t, *J* 6.0, 1′, 5′-H_2), 4.75 (1H, br s, 4-OH), 6.40 (1H, dd, *J* 7.5, 1.0, 5-H), 6.44 (1H, dd, *J* 8.0, 1.0, 7-H) and 6.66 (1H, t, *J* 7.8, 6-H).

Acknowledgements

This project was supported by NSFC, Natural Science Foundation of Hebei Province (297065) and the Science and Technology Commission of Hebei Province. B. L. would like to thank the Department of Chemistry, Cangzhou normal College, for leave of absence.

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Paper 8/05464I