JOURNAL OF CHEMICAL RESEARCH 2010 JUNE, 325–329 **RESEARCH PAPER** 325

Acid catalysed reaction of indanones, tetralones and benzosuberone with neopentyl glycol and other alkanediols under forced conditions

Masao Imai[a], Goreti Ribeiro Morais[b,d], Bassam al-Hindawi[c], Mazen A. M. al-Sulaibi[c], Mohammad Meetani[c] and Thies Thiemann[a,c]*

[a] *Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1, Kasuga-koh-en, Kasuga-shi 816-8580, Japan*
[b] *Faculty of Pharmacy, University of Lisbon, Av. Forças Armadas, P-1649 Lisboa, Portugal*
[c] *Department of Chemistry, Faculty of Science, United Arab Emirates University, PO Box 17551, Al Ain, UAE.*
[d] *Present address: Instituto Tecnologico e Nuclear, Estrada Nacional 10, Sacavem, Portugal*

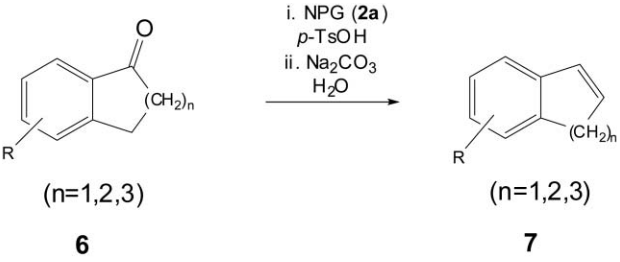
Upon reaction with an excess of 2,2-dimethylpropane-1,3-diol (neopentyl glycol, NPG) under acid catalysis, indanones and tetralones yield indenes and dihydronaphthalenes, respectively. The reaction can also be carried out with butane-1,3-diol.

Keywords: indanones, tetralones, indenes, 1,2-dihydronaphthalenes, alkene synthesis

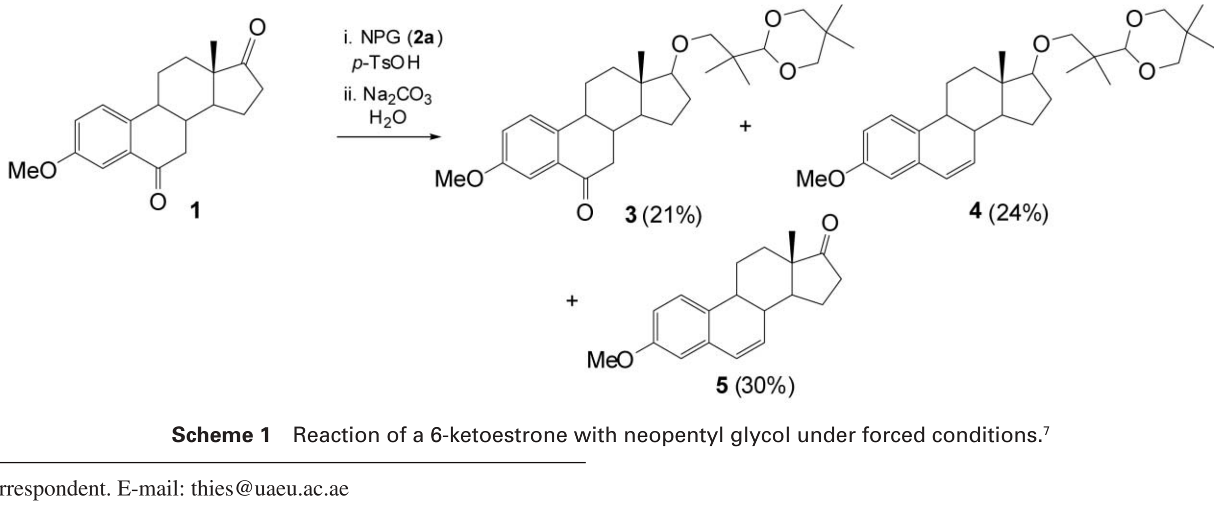
The protection of the keto function as a cyclic acetal through its reaction with glycerols is widely used.[1] 2,2-Dimethylpropane-1,3-diol (neopentyl glycol, NPG, **2a**) is a typical glycol which is used in such a transformation, and where 5,5-dimethyl-1,3-dioxanes[2,3] are obtained as the protected compounds. In the preparation of acetals derived from steroidal ketones with neopentyl glycol,[4–6] under forced, acidic conditions, and when using long reaction times, 17-*O*-[2′,2′-dimethyl-2′-(5″,5″-dimethyl-1″,3″-dioxanyl)ethyl] substituted estra-3,17β-diols are produced,[7] in which the original 17-keto function has undergone a formal reduction (Scheme 1). Vuligonda *et al.*[8] have also described an acid catalysed conversion of a number of α-tetralones to dihydronaphthalenes, where pentane-2,4-diol (**2c**) was used as reactant, again under long reaction times. Both reactions were explained by a reductive hydride transfer to the ketone as key mechanistic step.[7,8] Consequently, we have studied the reaction of benzylic ketones with neopentyl glycol and other alkanediols and have found that α-benzocycloalkenones in general form benzocycloalkadienes, when they are subjected to reactions with neopentyl glycol and with butane-1,3-diol using acid catalysis under forced conditions. The transformation is the subject of this communication.

Reaction of estrones with neopentyl glycol (NPG, **2a**) in refluxing benzene with the azeotropic removal of the water which was formed gives the corresponding acetals in good yield within 30 min. However, when 6-keto estrone **1** was heated with an excess amount of neopentyl glycol in refluxing benzene or in toluene using long reaction times, 17-*O*-[2′, 2′-dimethyl-2′-(5″,5″-dimethyl-1″,3″-dioxanyl)ethyl] steroidal ethers **4** and **5** as well as estra-1,3,5(10),6-tetraene (**6**) were formed (Scheme 1, see also ref. 7). The occurrence of estra-1,3,5(10),6-tetraenes **5** and **6** indicate that a neopentyl glycol reacts with a benzylic ketone in a similar maner to that which had been reported by Vuligonda *et al.* with pentane-1,3-diol (**2c**).[8]

In general, we have found that replacing the quaternary sp^3-hybridised carbon adjacent to the carbonyl group as in the steroidal series with an sp^2-hybridised carbon as in the case of α-benzocycloalkenones alterss the course of the reaction and leads, under forced conditions, to benzocycloalkadienes instead of to the [2′,2′-dimethyl-2′-(5″,5″-dimethyl-1″,3″-dioxanyl)ethyl]- substituted derivatives (*e.g.*, to **3**) (Scheme 2, Table 1). Mechanistically, it is possible, however, that in both cases there is an initial hydride shift from the alcohol component to the keto functionality (see below and Scheme 3). The reaction of 1-tetralones **6f–i** with NPG with *p*-TsOH catalysis has been found to give 1,2-dihydronaphthalenes **7f–i**. Indan-1-ones **6a–e** reacted comparably well to indenes **7a–e** whilst benzosuberone (**6j**) gave benzocycloheptadiene **7j** (Table 1).



Scheme 2 Reaction of a benzocycloalkanones with neopentyl glycolunder forced conditions.

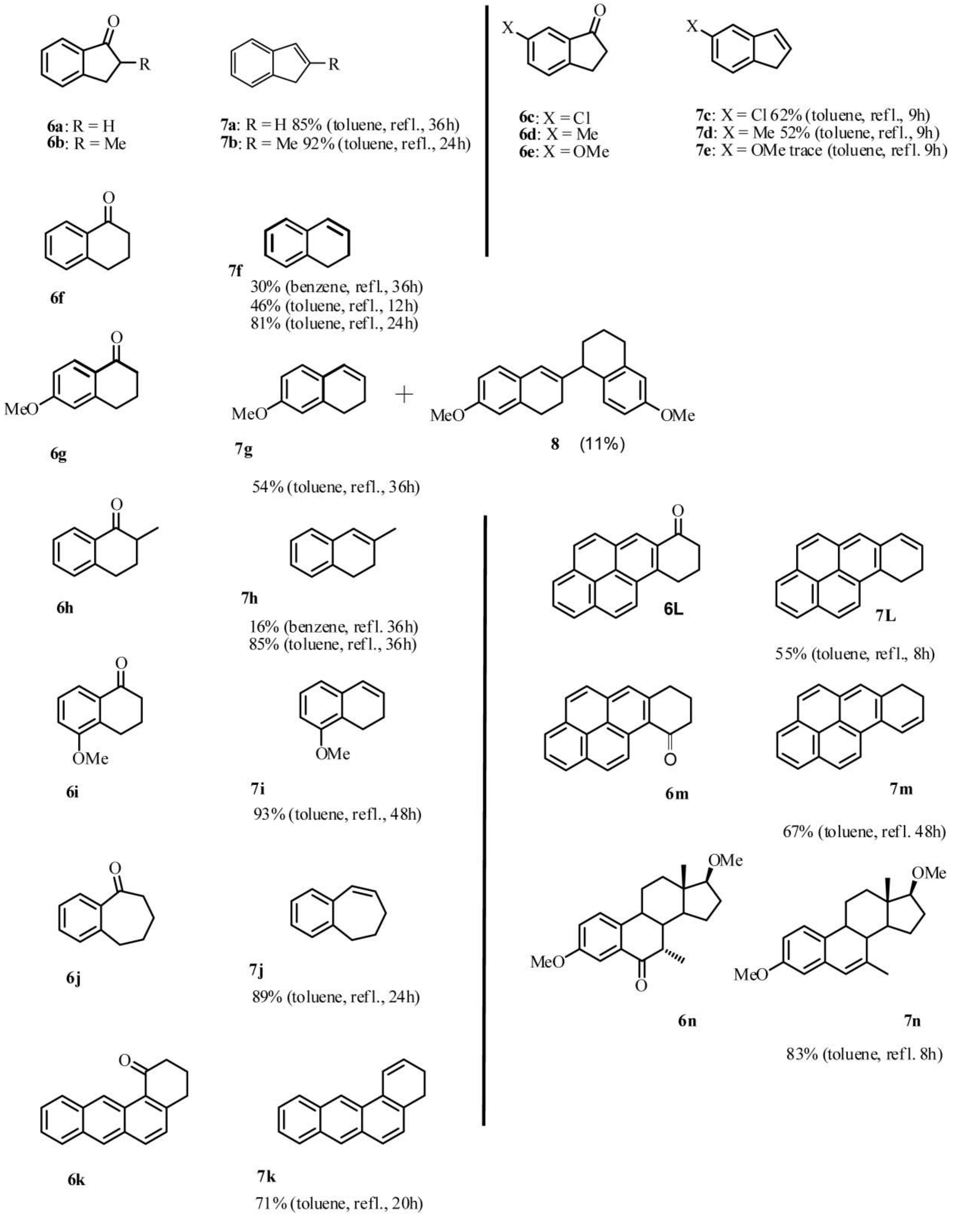


Scheme 1 Reaction of a 6-ketoestrone with neopentyl glycol under forced conditions.[7]

---

* Correspondent. E-mail: thies@uaeu.ac.ae

Table 1 Reaction of benzocycloalkanones with NPG (**2a**) under forced acidic conditions



6a: R = H
6b: R = Me

7a: R = H 85% (toluene, refl., 36h)
7b: R = Me 92% (toluene, refl., 24h)

6c: X = Cl
6d: X = Me
6e: X = OMe

7c: X = Cl 62% (toluene, refl., 9h)
7d: X = Me 52% (toluene, refl., 9h)
7e: X = OMe trace (toluene, refl. 9h)

6f

7f
30% (benzene, refl., 36h)
46% (toluene, refl., 12h)
81% (toluene, refl., 24h)

6g

7g + **8** (11%)
54% (toluene, refl., 36h)

6h

7h
16% (benzene, refl. 36h)
85% (toluene, refl., 36h)

6i

7i
93% (toluene, refl., 48h)

6j

7j
89% (toluene, refl., 24h)

6k

7k
71% (toluene, refl., 20h)

6L

7L
55% (toluene, refl., 8h)

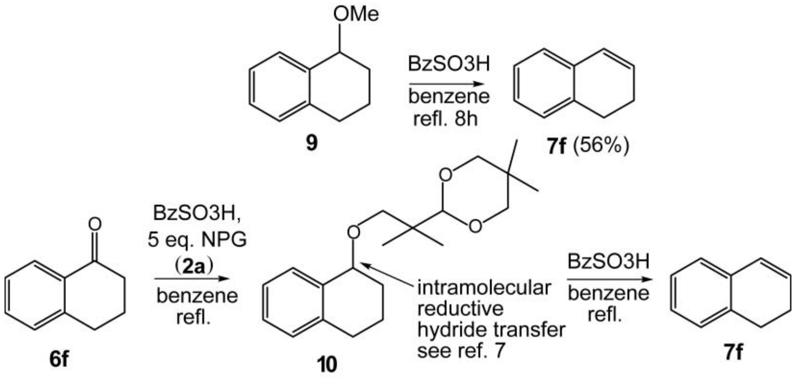
6m

7m
67% (toluene, refl. 48h)

6n

7n
83% (toluene, refl. 8h)

A possible mechanism for the reaction can be formulated with [2′,2′-dimethyl-2′-(5″,5″-dimethyl-1″,3″-dioxanyl)ethyl]tetrahydronaphthols **10** as intermediates, where a subsequent acid catalysed elimination reaction would lead to the products (Scheme 3). It must be stated, however, that 1-[2′,2′-dimethyl-2′-(5″,5″-dimethyl-1″,3″-dioxanyl)ethyl]-1,2,3,4-tetrahydronaphthol **10** could not be isolated under the reaction conditions, whle the reaction proceeded to give the corresponding olefins in good yield, and thus the potential intermediacy of these compounds could not be confirmed. Only in the case of the 5-methoxyindanone (**6e**), which gave the corresponding 5-methoxyindene (**7e**) in very poor yield, was the ether-acetal detected by ^{1}H NMR analysis of the reaction mixture. That a benzyl cation is involved in the final step of the transformation may be noted by the isolation of side products, such as dimer **8**, which may be formed by reaction of the stabilised benzyl cation with dihydronaphthalene (**7g**). That an 1-alkoxy-1,2,3,4-tetrahydronapthalene is easily converted to a 1,2-dehydronapthalene under the conditions was shown by the acid catalysed reaction of 1-methoxy-1,2,3,4-tetrahydronaphthalene (**9**) to give 1,2-dihydronaphthalene (**7f**).



Scheme 3 Tentative mechanism for the formation of dihydronaphthalene (**7f**) from 1-tetralone via ether-acetal (**10**).

Not only is the electronic character of the aromatic ring of the α-benzocycloalkenone important for the outcome of the overall reaction, where overt stabilisation of a benzylic cation intermediate by an electron rich benzo group leads to dimeric side-products, but also the nature of the substituent at the β-position is important. Here, an alkyl substituent such as a methyl group has been found to be advantageous. Suitable substrates include the higher-annelated systems **6k–m**. However, the acid-catalysed transformation of benzothiophenone **11** does not give the corresponding acetal. In this case, two alkoxybenzo[*b*]thiophenes, **12a** and **12b**, were isolated from the reaction, signalling the dominant contribution of the hydroxybenzothiophene tautomer (Scheme 4).

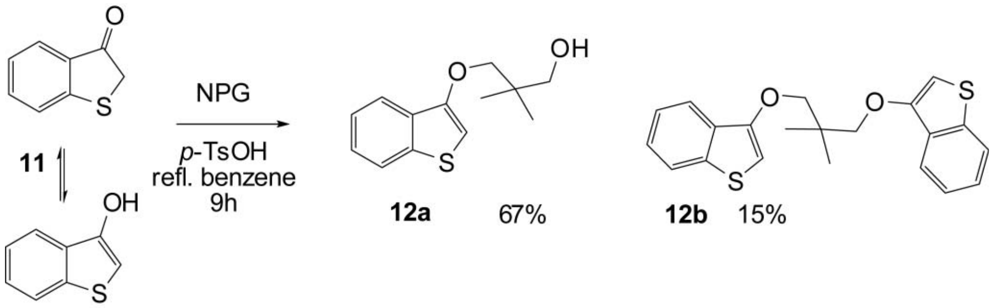
The reaction discussed above proceeds equally well with butane-1,3-diol (**2b**) (Table 2), although ethane-1,2-diol cannot be used. With the latter, the ketones are recovered, after water is added to the reaction mixture upon termination of the reaction. Reactions of **6g** with neopentyl glycol (**2a**), butane-1,3-diol (**2b**), and pentane-2,4-diol (**2c**) gave the product **7g** in almost identical yield (Table 2). No product was formed with butane-1,2,4-triol, and only a trace of alkene is formed with butan-1,2,-diol.

In summary, it has been found that 1-indanones, 1-tetralones, and benzosuberone can be converted to indenes, 1,2-dihydronapthalenes, and benzocycloheptadiene when heated with butane-1,3-diol (**2b**) or with neopentyl glycol (**2a**) under acid catalysis. The reaction is a good alternative to the classic reduction, dehydration protocol. This is particularly the case in the preparation of estra-1,3,5(10),6-tetraenes from the readily accessible 6-ketoestra-1,3,5(10)-trienes which is usually carried out by reduction–dehydration[4,6] or by a two step Shapiro reaction.[7] Lastly, the direct access of 9,10-dihydrobenzo[a]pyrene (**7l**) from commercial 9,10-dihydrobenzo[a]pyren-7(8*H*)-one (**6l**) and the complementary access of 7,8-dihydrobenzo[a]pyrene (**7m**) from 7,8-dihydrobenzo [a]pyren-10(9*H*)-one (**6m**), coupled with the easy availability of **6m** by a surprising site-selective oxidation of 7,8,9,10-tetra hydrobenzo[a]pyrene, provide important starting materials for the synthesis of dihydrodiols of polycyclic aromatic hydrocarbons.[9]

Experimental

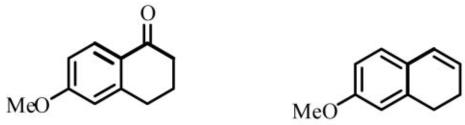
Melting points were measured on a Yanaco microscope hotstage and are uncorrected. IR spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ2OM instruments. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL EX-270 spectrometer (^{1}H at 270 MHz, ^{13}C at 67.8 MHz), a JEOL Lambda 400 FT-NMR spectrometer (^{1}H at 395.7 MHz, ^{13}C at 99.45 MHz), a Varian 200 MHz NMR spectrometer (^{1}H at 200 MHz), and a Varian 400 MHz NMR spectrometer (^{1}H at 399.7 MHz, ^{13}C at 100.5MHz). The assignments of the carbon signals were aided by DEPT 90 and DEPT 135 experiments (DEPT = Distortionless Enhancement by Polarisation Transfer). Here, (–) denotes secondary carbons, (+) primary or tertiary carbons and (C_{quat}) quaternary carbons. The chemical shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). Mass spectra were measured with a JMS-01-SG-2 spectrometer and with an Agilent 6310 Ion Trap. Column chromatography was carried out on Wakogel 300. Ketones **6a**, **6c–g**, **6i–l** were acquired commercially. Ketones **6b** and **6h** were prepared by α-methylation of ketones **6a** and **6f**, respectively. **6m** was synthesised by site-selective oxidation of 7,8,9,10-tetrahydrobenzo[a]pyrene ($KMnO_4$, PTC), itself available through hydrogenation of **7l**. 1-Methoxytetrahydronaphalene (**9**) (KOH, MeI, DMSO)[10] and 5-bromo-6-methoxy-1-tetralone (**6o**) (NBS, H_2O, H_2SO_4)[11] were synthesised according to known procedures. **6n** was prepared by oxidation of the benzylic position of di-*O*- methylestra-1,3,5(10)-trien-3,17β-diol ($KMnO_4$, PTC) and subsequent conjugate addition of methyl iodide to its enolate, in a manner earlier described.[4,5] 5-(4-Docosanyloxyphenyl)-6-methoxytetral-1-one (**6p**) was prepared by Suzuki-Miyaura reaction of **6o** and the respective 4-docosanyloxyphenylboronic acid [dioxane, $(PPh_3)_2PdCl_2$, 2 equiv. PPh_3, aq. Na_2CO_3], where the boronic acids was synthesised from the corresponding *p*-docosanyloxybromobenzene (a. *n*-BuLi, $B(OR)_3$, THF; b. HCl).[12]

Indene (**7a**): A solution of 1-indanone (**6a**, 500 mg, 3.8 mmol), neopentyl glycol (**2a**, 1.53 g, 15.6 mmol) and *p*-toluenesulfonic acid (100 mg) in benzene (6 mL) was stirred at 80 C for 24h. Thereafter, a saturated aq. Na_2CO_3 solution (5 mL) was added, and the mixture was extracted with ether (3 x 20 mL). The ether was removed carefully, and the residue was subjected to a bulb-to-bulb distillation using a glass tube oven (model GTO-258S SIBATA) to yield indene (**7a**,



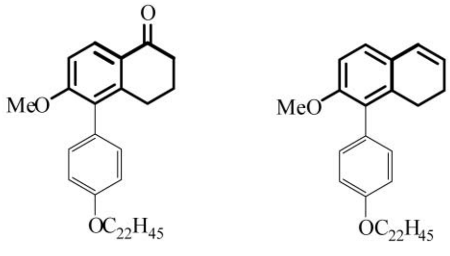
Scheme 4

Table 2 Reaction using different alkanediols



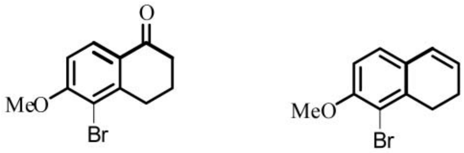
6g **7g**

NPG (**2a**), *p*-TsOH: 54% (toluene, refl., 36h)
butane-1,3-diol (**2b**), $BzSO_3H$: 65% (benzene, refl., 22h)
pentane-2,4-diol (**2c**), $BzSO_3H$: 67% (benzene, refl., 22h)



6p **7p**

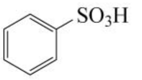
butane-1,3-diol (**2b**), $BzSO_3H$: 75% (benzene, refl., 13h)
pentane-2,4-diol (**2c**), $BzSO_3H$: 73% (benzene, refl., 13h)



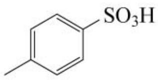
6o **7o**

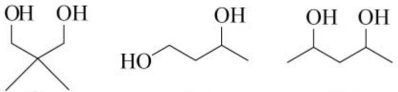
butane-1,3-diol (**2b**), $BzSO_3H$: 68% (benzene, refl., 15h)
pentane-2,4-diol (**2c**), $BzSO_3H$: 68% (benzene, refl., 15h)

$BzSO_3H$:



p-TsOH:





2a **2b** **2c**

375 mg, 85%) as a colourless oil; (neat/cm^{-1})ν_{max} 3054, 3025, 2890, 1460, 1395, 766, 720, 695; δ_H (270 MHz, $CDCl_3$) 3.39 (2H, bs), 6.55 (1H, d, ^3J = 5.7 Hz), 6.88 (1H, dm, ^3J = 5.7 Hz), 7.19 (1H, m), 7.26 (1H, m), 7.40 (1H, d, ^3J = 7.4 Hz), 7.46 (1H, d, ^3J = 9.0 Hz); δ_C (67.8 MHz, $CDCl_3$) 39.0, 121.0, 123.7, 124.5, 126.3, 132.1, 134.0, 143.7, 144.8; MS (EI, 70 eV) *m/z* (%) 116 (M^+, 95).

2-Methylindene (**7b**): Colourless oil. (Found: M^+, 130.0784. $C_{10}H_{10}$ requires M^+, 130.0783). (neat/cm^{-1}) ν_{max} 2924, 1459, 1354, 1175, 1107, 826, 749, 715; δ_H 2.15 (3H, s, CH_3), 3.28 (2H, s), 6.48 (1H, s), 7.08 (1H, m), 7.17–7.25 (2H, m), 7.35 (1H, d, ^3J = 7.3 Hz); δ_C 16.7 (CH_3), 42.7 (–), 119.7 (CH), 123.3 (CH), 123.5 (CH), 126.2 (CH), 127.2 (CH), 143.3 (C_{quat}), 145.9 (C_{quat}), 146.0 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 130 (100) [M^+], 115 (70) [M^+-CH_3].

5-Chloroindene (**7c**): Colourless oil. (Found: M^+, 150.0236. $C_9H_7{}^{35}Cl$ requires M^+, 150.0236). (neat/cm^{-1}) ν_{max} 3066, 2892, 1605, 1551, 1460, 1390, 1077, 946, 891, 869, 805, 692, 678; δ_H (270 MHz, $CDCl_3$) 3.37 (2H, s), 6.61 (1H, dt, ^3J = 5.7 Hz, ^3J = 1.9 Hz), 6.82 (1H, dm, ^3J = 5.7 Hz), 7.15 (1H, dd, ^3J = 8.1 Hz, ^4J = 1.9 Hz), 7.36 (1H, d, ^3J = 8.1 Hz), 7.37 (1H, d, ^4J = 1.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 38.7 (CH_2), 121.1 (CH), 124.4 (CH), 124.5 (CH), 131.3 (CH), 132.2 (C_{quat}), 136.0 (C_{quat}), 141.8 (CH), 146.6 (C_{quat}); MS (EI, 70 eV) *m/z* (%) 152 ([^{37}Cl]M^+, 13), 150 ([^{35}Cl]M^+, 48).

5-Methylindene (**7d**): Colourless oil. (Found: M^+, 130.0782. $C_{10}H_{10}$ requires M^+, 130.0783). (neat/cm^{-1}) ν_{max} 3060, 3022, 2918, 1621, 1557, 1495, 1473, 1393, 945, 914, 803, 729, 693; δ_H 2.48 (3H, s, CH_3), 3.35 (2H, bs), 6.53 (dt, 1H, ^3J = 5.7 Hz, ^3J = 1.9 Hz), 6.82 (1H, dm, ^3J = 5.7 Hz), 7.00 (1H, d, ^3J = 7.6 Hz), 7.18 (1H, s), 7.35 (1H, d, ^3J = 7.6 Hz); δ_C 21.1 (CH_3), 38.4 (–), 121.6 (CH), 123.1 (CH), 125.2 (CH), 131.8 (CH), 134.7 (CH), 135.6 (C_{quat}), 140.4 (C_{quat}), 152.9 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 130 (100) [M^+].

1,2-Dihydronapthalene (**7f**): Colourless oil. (neat/cm^{-1}) ν_{max} 3030, 2932, 2882, 2929, 1486, 1453, 1427, 1277, 1094, 1030, 1026, 1009, 780, 745, 691, 581; δ_H (270 MHz, $CDCl_3$) 2.29–2.35 (2H, m), 2.79 (2H, t, ^3J = 8.1 Hz), 6.01 (1H, dt, ^3J = 9.5 Hz, ^3J = 4.9 Hz), 6.45 (1H, d, ^3J = 9.5 Hz), 7.00 (1H, m), 7.08–7.14 (3H, m); δ_C (67.8 MHz, $CDCl_3$) 23.2 (CH_2), 27.5 (CH_2), 125.9 (CH), 126.4 (CH), 126.8 (CH), 127.5 (CH), 127.8 (CH), 128.6 (CH), 134.1 (C_{quat}), 135.5 (C_{quat}); MS (EI, 70 eV) *m/z* (%) 130 (97).

7-Methoxy-1,2-dihydronaphthalene (**7g**): Colourless oil. (Found: M^+, 160.0890. $C_{11}H_{12}O$ requires M^+, 160.0888). (neat/cm^{-1}) ν_{max} 3030, 2934, 2832, 1601, 1574, 1468, 1434, 1344, 1265, 1237, 1096, 1080, 803, 783, 700; δ_H (270 MHz, $CDCl_3$) 2.28–2.33 (2H, m), 2.79 (2H, dd, ^3J = 8.6 Hz, ^3J = 8.4 Hz), 3.83 (3H, s, OCH_3), δ_C (67.8 MHz, $CDCl_3$) 19.4 (–), 22.6 (–), 55.5 (+, OCH_3), 109.6 (CH), 118.9 (CH), 123.1 (C_{quat}), 126.6 (CH), 127.6 (CH), 128.8 (CH), 135.1 (C_{quat}), 156.1 (C_{quat}); MS (EI, 70 eV) *m/z* (%) 160 (M^+) (100).

7-Methoxy-3-(6′-methoxy-1′,2′,3′,4′-tetrahydronaphth-1′-yl)-1,2-dihydronaphthalene (**8**): Off-white solid; (Found: M^+, 320.1770. $C_{22}H_{24}O_2$ requires M^+, 320.1776). δ_H (270 MHz, $CDCl_3$) 1.73–1.77 (2H, m), 1.89–1.93 (2H, m), 2.10–2.13 (2H, m), 2.70–2.77 (4H, m), 3.58 (1H, s), 3.78 (3H, s, OCH_3), 3.79 (3H, s, OCH_3), 6.14 (1H, s), 6.64–6.68 (4H, m), 6.91 (1H, d, ^3J = 8.9 Hz), 7.09 (1H, d, ^3J = 8.1 Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 21.4 (–), 24.9 (–), 28.8 (–), 29.1 (–), 30.2 (–), 46.5 (+, CH), 55.2 (+, OCH_3), 55.3 (+, OCH_3), 111.1 (+, CH), 112.0 (+, CH), 113.4 (+, CH), 113.5 (+, CH), 124.2 (+, CH), 126.4 (+, CH), 128.1 (C_{quat}), 128.3 (C_{quat}), 130.3 (+, CH), 136.5 (C_{quat}), 138.9 (C_{quat}), 143.1 (C_{quat}), 157.7 (C_{quat}), 158.2 (C_{quat}); MS (EI, 70 eV) *m/z* (%) 320 (M^+) (100), 160 (98).

3-Methyl-1,2-dihydronaphthalene (**7h**): Colourless oil. (Found: M^+, 144.0935. $C_{11}H_{12}$ requires M^+, 144.0939). (neat/cm^{-1}) ν_{max} 3062, 3016, 2962, 2924, 2880, 1652, 1604, 1486, 1441, 1109, 1019, 974, 875, 842, 752, 729; δ_H (270 MHz, $CDCl_3$) 1.90 (3H, s, CH_3), 2.23 (2H, dd, ^3J = 8.4 Hz, ^3J = 8.1 Hz), 2.81 (2H, dd, ^3J = 8.4 Hz, ^3J = 8.1 Hz), 6.21 (1H, d, ^4J = 2.1 Hz), 6.94 (1H, d, ^3J = 7.0 Hz), 7.02–7.25 (3H, m); δ_C (67.8 MHz, $CDCl_3$) 23.5 (CH_3), 28.1 (–), 28.8 (–), 122.7 (CH), 125.1 (CH), 125.9 (CH), 126.3 (CH), 127.1 (CH), 128.2 (C_{quat}), 135.0 (C_{quat}), 138.2 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 144 (50) [M^+], 129 (100) [M^+-CH_3].

8-Methoxy-1,2-dihydronaphthalene (**7i**): Colourless oil. (Found: M^+, 160.0887. $C_{11}H_{12}O$ requires M^+, 160.0888). (neat/cm^{-1}) ν_{max} 3028, 2932, 2830, 1609, 1570, 1501, 1464, 1427, 1394, 1305, 1277, 1250, 1152, 1122, 1108, 1038, 818, 568; δ_H (270 MHz, $CDCl_3$) 2.27–2.30 (2H, m), 2.77 (2H, t, ^3J = 8.4 Hz), 3.78 (3H, s, OCH_3), 5.88 (dt, 1H, ^3J = 9.5 Hz, ^3J = 4.6 Hz), ^3J = 6.40 (1H, d, ^3J = 9.5 Hz), 6.67–6.70 (2H, m), 6.93 (1H, d, ^3J = 8.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 23.0 (–), 28.0 (–), 55.2 (OCH_3), 111.1 (CH), 113.8 (CH), 125.9 (CH), 126.8 (CH), 127.1 (CH), 127.4 (C_{quat}), 137.2 (C_{quat}), 158.6 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 160 (M^+) (100), 145 (42), 115 (52).

Benzocycloheptadiene (benzosuberene, **7j**):[13] Colourless oil. (Found: M^+, 144.0936. $C_{11}H_{12}$ requires M^+, 144.0939). δ_H (270 MHz,

$CDCl_3$) 1.83–1.65 (2H, m), 2.15–2.30 (2H, m), 2.72–2.84 (2H, m), 5.75 (1H, dt, $^3J = 11.9$ Hz, $^4J = 3.9$ Hz), 6.33 (1H, dt, $^3J = 11.9$ Hz, $^4J = 1.9$ Hz), 7.09–7.11 (4, m); MS (EI, 70 eV) *m/z* (%) = 144 (M^+) (36), 129 (100).

3,4-Dihydrobenzo[a]anthracene (**7k**):[14] (Found: M^+, 230.1098. $C_{18}H_{14}$ requires M^+, 230.1096). ν_{max} (KBr/cm^{-1}) 1656, 1540, 875, 740, 706, 679; δ_H (270 MHz, $CDCl_3$) 2.42–2.44 (2H, m), 2.97 (2H, t, $^3J = 8.7$ Hz), 6.31 (1H, dt, $^3J = 10.0$ Hz, $^3J = 4.9$ Hz), 7.28 (1H, d, $^3J = 8.6$ Hz), 7.41–7.45 (3H, m), 7.83 (1H, d, $^3J = 8.6$ Hz), 7.94–7.99 (2H, m), 8.36 (1H, s), 8.63 (1H, s); δ_C (67.8 MHz, $CDCl_3$) 22.9 (CH_2), 28.5 (CH_2), 120.8 (CH), 123.3 (CH), 125.1 (CH), 125.3 (CH), 126.7 (CH), 127.0 (CH), 127.1 (CH), 127.9 (CH), 128.3 (C_{quat}), 128.4 (C_{quat}), 128.5 (CH), 129.0 (CH), 130.9 (C_{quat}), 131.4 (C_{quat}), 131.8 (C_{quat}), 132.3 (C_{quat}), MS (EI, 70 eV) *m/z* (%) = 230 (100) [M^+], 215 (22).

9,10-Dihydrobenzo[a]pyrene (**7l**):[15] Colourless solid, m.p. 146 °C. (Found: M^+, 254.1098. $C_{20}H_{14}$ requires M^+, 254.1096). (KBr/cm^{-1}) ν_{max} 3028, 2926, 2874, 2824, 1598, 1438, 1418, 1297, 1180, 882, 840, 823, 705, 682; δ_H 2.53–2.61 (2H, m), 3.49 (2H, dd, $^3J = 8.2$ Hz, $^3J = 8.1$ Hz), 6.25 (1H, dt, $^3J = 9.7$ Hz, $^3J = 3.9$ Hz), 6.84 (1H, d, $^3J = 9.7$ Hz), 7.84 (1H, s), 7.90–8.12 (6H, m), 8.25 (1H, d, $^3J = 9.4$ Hz); δ_C 23.3 (2C), 123.0, 123.2, 124.6, 124.8, 125.0, 125.6, 126.7, 127.5, 128.0 (2C), 128.3, 128.7, 129.3, 129.6, 129.7, 130.7, 131.3, 131.9; MS (EI, 70 eV) *m/z* (%) = 254 (100) [M^+], 239 (23).

7,8-Dihydrobenzo[a]pyrene (**7m**):[9] Colourless solid, mp. 127 °C. (Found: M^+, 254.1100. $C_{20}H_{14}$ requires M^+, 254.1096). (KBr/cm^{-1}) ν_{max} 1176, 883, 839, 827, 775, 756, 730, 704, 677; δ_H 2.47–2.54 (2H, m), 3.23 (2H, dd, $^3J = 8.1$ Hz, $^3J = 7.8$ Hz), 6.41 (1H, dt, $^3J = 10.0$ Hz, $^3J = 4.9$ Hz), 7.55 (1H, d, $^3J = 10.0$ Hz), 7.91–8.14 (7H, m), 8.35 (1H, d, $^3J = 9.4$ Hz); δ_C 23.1 (–), 29.1 (–), 122.3 (CH), 123.8 (CH), 124.5 (CH), 124.7 (CH), 125.0 (CH), 125.1 (C_{quat}), 125.5 (CH), 126.0 (C_{quat}), 126.9 (CH), 127.2 (CH), 127.4 (CH), 128.0 (C_{quat}), 129.3 (C_{quat}), 130.1 (C_{quat}), 130.5 (CH), 130.7 (C_{quat}), 131.2 (C_{quat}), 134.1 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 254 (100) [M^+].

3,17-Di-(O-methyl)-7-estra-1,3,5(10),6-tetraen-3,17β-diol (**7n**): Colourless solid; m.p. 121 °C; (Found: M^+, 312.2089. $C_{21}H_{28}O_2$ requires M^+, 312.2089). (KBr/cm^{-1}) ν_{max} 2924, 2848, 1605, 1500, 1459, 1266, 1202, 1105, 1039, 871; δ_H (270 MHz, $CDCl_3$) 0.78 (3H, s, CH_3), 1.30–2.45 (11H, m), 1.96 (3H, s, CH_3), 3.25 (1H, m), 3.38 (3H, s, CH_3), 3.78 (3H, s, CH_3), 6.20 (1H, s), 6.56 (1H, d, $^4J = 2.7$ Hz), 6.68 (1H, dd, ^3J 8.4 Hz, $^4J = 2.7$ Hz), 7.16 (1H, d, $^3J = 8.4$ Hz); δ_C (67.8 MHz, $CDCl_3$) 11.5, 24.5 (2C), 26.9, 27.5, 36.7, 41.8, 42.1, 44.8, 47.3, 55.3, 57.9, 89.7, 110.4, 111.0, 124.34, 125.3, 131.4, 135.9, 143.7, 158.2; MS (EI, 70 eV) *m/z* (%) 312 (M^+, 23).

5-Bromo-6-methoxy-1,2-dihydronaphthalene (**7o**): Off-white solid; δ_H (200 MHz, $CDCl_3$) 2.27–2.79 (2H, m), 2.89 (2H, dd, $^3J = 8.6$, $^3J = 8.2$ Hz), 3.86 (3H, s, OCH_3), 5.86–5.93 (1H, m), 6.33 (1H, d, $^3J = 9.8$ Hz), 6.67 (1H, d, $^3J = 8.2$ Hz), 6.90 (1H, d, $^3J = 8.2$ Hz); δ_C (50.3 MHz, $CDCl_3$) 22.5 (CH_2), 27.3 (CH_2), 55.8 (OCH_3), 108.6 (CH), 111.2 (C_{quat}), 124.9 (CH), 125.9 (CH), 126.2 (CH), 128.3 (C_{quat}), 136.2 (C_{quat}), 154.6 (C_{quat}); MS: 241.0 ($^{81}BrMH^+$), 239.0 ([^{79}Br]MH^+)

5-(4-Docosanyloxyphenyl)-6-methoxy-1,2-dihydronaphthalene (**7p**): Colourless solid; m.p. 88 °C. (KBr/cm^{-1}) 3033, 2920, 2849, 1607, 1571, 1512, 1472, 1239, 1175, 1065, 826, 718, 589; δ_H (400 MHz, $CDCl_3$) 0.88 (3H, t, $^3J = 6.8$ Hz, CH_3), 1.24–1.27 (36H, m), 1.46 (2H, m), 1.78–1.82 (2H, m), 2.12–2.18 (2H, m), 2.52 (2H, t, $^3J = 8.0$ Hz), 3.71 (3H, s, OCH_3), 3.99 (2H, t, $^3J = 6.8$ Hz, OCH_2), 5.90 (dt, 1H, $^3J = 9.6$ Hz, $^3J = 4.4$ Hz), 6.47 (dt, 1H, $^3J = 9.6$ Hz, $^4J = 1.8$ Hz), 6.76 (1H, d, $^3J = 8.4$ Hz), 6.94 (2H, d, $^3J = 8.8$ Hz), 7.00 (1H, d, $^3J = 8.4$ Hz), 7.12 (2H, d, $^3J = 8.8$ Hz); δ_C (100.5 MHz, $CDCl_3$) 14.1 (CH_3), 22.7 (CH_2), 23.0 (CH_2), 25.4 (CH_2), 26.1 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 29.7 (15C, CH_2), 31.9 (CH_2), 55.7 (OCH_3), 67.9 (OCH_2), 108.2 (CH), 113.9 (2C, CH), 125.8 (CH), 126.1 (CH), 127.5 (C_{quat}), 127.6 (CH), 128.9 (C_{quat}), 129.5 (C_{quat}), 131.2 (2C, CH), 135.5 (C_{quat}), 156.4 (C_{quat}), 158.0 (C_{quat}); MS 561.5 (MH^+).

3-(3-Hydroxy-2,2-dimethyl-propyloxy)-benzo[b]thiophene (**12a**): Colourless solid; m.p. 93 °C. (Found: M^+, 236.0869. $C_{13}H_{16}O_2S$ requires M^+, 236.0871). (KBr/cm^{-1}) ν_{max} 3850 (bs, OH), 2960, 2870, 1572, 1530, 1466, 1439, 1378, 1352, 1181, 1161, 1138, 1120, 1046, 1013, 866, 760, 732; δ_H 1.10 (6H, s, 2 CH_3), 3.61 (2H, bs), 3.94 (2H, s), 6.31 (1H, s), 7.34–7.39 (2H, m), 7.73–7.79 (2H, m); δ_C 21.7 (2C, CH_3), 36.6 (C_{quat}), 69.7 (–), 96.2 (CH), 120.8 (CH), 122.9 (CH), 123.7 (CH), 125.2 (CH), 133.2 (C_{quat}), 137.7 (C_{quat}), 150.9 (C_{quat}); MS (EI, 70 eV) *m/z* (%) 236 (17) [M^+], 150 (100), 121 (20).

1,3-(2,2,-Dimethyl)propyl bis(benzo[b]thien-3-yl) ether (**12b**): Colourless solid; m.p. 83 °C. (Found: M^+, 368.0904. $C_{21}H_{20}O_2S_2$ requires M^+, 368.0905). (KBr/cm^{-1}) ν_{max} 3116, 2912, 1572, 1530, 1460, 1433, 1351, 1179, 1161, 1138, 1118, 867, 798, 758, 717; δ_H (270 MHz, $CDCl_3$) 1.29 (6H. s, 2 CH_3), 4.07 (4H, s), 6.31 (2H, s), 7.30–7.37 (4H, m), 7.71–7.82 (4H, m); δ_C 22.1 (2C, CH_3), 36.3 (|C_{quat}), 75.2 (2C, -), 96.1 (2C, CH), 120.9 (2C, CH), 122.8 (2C, CH), 123.6 (2C, CH), 125.2 (2C, CH), 132.2 (2C, C_{quat}), 137.6 (2C, C_{quat}), 151.0 (2C, C_{quat}); MS (EI, 70 eV) 368 (65) [M^+], 219 (31), 150 (100), 121 (76).

Ms. Y. Tanaka is thanked for MS and HRMS measurements of many of the compounds.

Received 11 April 2010; accepted 15 May 2010
Paper 1000065 doi: 10.3184/030823410X12753214605445

References

1 T.W. Greene and P.G.M. Wuts, *Protective groups in organic synthesis*, 2nd edn, John Wiley & Sons, N.Y. 1991, pp. 185.
2 E. Piers, J. Banville, C.K. Lau and I. Nagakura, *Can. J. Chem.*, 1982, **60**, 2965
3 M.A. Avery, C. Jennings-White and W.K.M. Chong, *Tetrahedron Lett.*, 1987, **28**, 4269.
4 G. Ribeiro Morais, M.C. das Neves Oliveira and T. Thiemann, *Lett. Org. Chem.*, 2006, **3**, 214.
5 T. Thiemann, K. Umeno, E. Inohae, M. Imai, Y. Shima, and S. Mataka, *J. Chem. Res.* (*S*), 2002, 1; (*M*), 2002, 101.
6 M.C. Melo e Silva, L. Patricio, L. Gano, M.L. Sa e Melo, E. Inohae, S. Mataka and T. Thiemann, *Appl. Rad. Isotop.*, 2001, **54**, 227.
7 C. Oliveira, G. Ribeiro Morais, M. Imai, E. Inohae, C. Yamamoto, S. Mataka, T. Thiemann, *J. Chem. Res.*, 2010, 158.
8 V. Vuligonda, Y. Lin and R.A.S. Chandraratna, *Tetrahedron Lett.*, 1996, **37**, 1941.
9 F. Oesch, G. Stillger, H. Frank and K.L. Platt, *J. Org. Chem.*, 1982, **47**, 568.
10 R.A.W. Johnstone and M.E. Rose, *Tetrahedron*, 1979, **35**, 2169.
11 I. Pravst, M. Zupana and S. Stavber, *Tetrahedron Lett.*, 2006, **47**, 4707.
12 *cf.*, K. Fuchibe and T. Akiyama, *J. Am. Chem. Soc.*, 2006, **128**, 1434.
13 R.W. Thies and R.H. Chiarello, *J. Org. Chem.*, 1979, **44**, 1342.
14 R.A. Lehr, M. Schaefer-Ridder and D.M. Jerina, *J. Org. Chem.*, 1977, **42**, 736.
15 S.A. Klassen, G.H. Daub and D.L. VanderJagt, *J. Org. Chem.*, 1983, **48**, 4361.