Pergamon

Tetrahedron 57 (2001) 1709–1713

TETRAHEDRON

Thallium trinitrate-mediated ring contraction of 1,2-dihydronaphthalenes: an approach to the synthesis of indans

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Received 13 November 2000; accepted 21 December 2000

Abstract—Oxidation of 1,2-dihydronaphthalenes with thallium trinitrate was studied. 1,2-dihydronaphthalene, 1-methyl-1,2-dihydronaphthalene, 6- and 8-methoxy-1,2-dihydronaphthalenes gave rise to the respective ring contraction products in good yields, whereas the rearrangement was not observed using 4-methyl-1,2-dihydronaphthalene and 1-*n*-butyl-4-methyl-1,2-dihydronaphthalene as substrates.

Thallium(III) salts oxidize a wide variety of different organic functionalities.[1] A useful transformation promoted by these salts is the ring contraction of simple cyclic olefins,[2] such as cyclobutene,[3] cyclohexenes,[4,5] cycloheptene[3,5] and cyclooctene.[3,5] Although this kind of transformation is well-known since the pioneer work of Kabbe,[4] the behavior of dihydronaphthalene derivatives toward thallium(III) salts has never been studied. The most similar substrates already studied were a few chromenes, which furnished either ring contraction products, in poor to moderate yields,[6] or glycolic derivatives.[7]

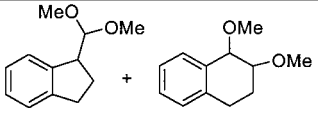
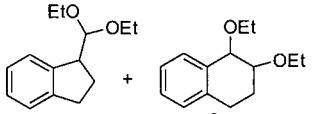
In our program directed towards the application of thallium(III) salts in the synthesis of natural and/or biologically active compounds,[8,9] we decided to investigate the reaction of a series of 1,2-dihydronaphthalenes with thallium trinitrate (TTN). Such a reaction could lead, in a single step, to indanic systems, which have the potential to be biologically active.[10]

This study was initiated by performing the reaction of 1,2-dihydronaphthalene (**1**) with TTN in methanol at room temperature. The ring contraction product **2** was obtained in 60% yield, together with 8% of *trans* and *cis*-1,2-dimethoxy-1,2,3,4-tetrahydronaphthalenes (**3a** and **3b**) (Table 1, entry 1). Acetal **2** was obtained in 77% yield at lower temperature (entry 2), which corroborates observations by Sekizaki et al.[11] Oxidation of **1** with TTN in ethanol also led to the rearrangement product (**4**) in good yield (entry 3).

Under the same reaction conditions, 1-methyl-1,2-dihydronaphthalene (**6**) led to the ring contraction product **11** in very good yield (Table 2, entry 1). Notably, the reaction occurred with complete diastereoselectivity, giving rise to the *trans* diastereoisomer, as deduced by NMR analysis and comparison with other indans data.[12] The *trans*-1,3 substituted indan system, which is not easily achieved by standard methods, is present in some natural products, such as mutisianthol and jungianol.[13]

Reacting 6- and 8-methoxy-1,2-dihydronaphthalenes (**7** and **8**, respectively) with TTN in methanol, the corresponding ring contraction products and glycolic derivatives were isolated, by column chromatography, in reasonable yields (entries 2 and 4). Since temperature lowering seems to favor the rearrangement (compare entries 1 and 2, Table 1), the reaction of **7** was also performed at −78°C, but the same

Table 1. Reaction of 1,2-dihydronaphthalene (**1**) with TTN

Entry	Conditions	Product (yield)
1	MeOH, rt, 1 min	 **2** (60%) + **3** (8%)
2	MeOH, 0 °C, 5 min	**2** (77%) --
3	EtOH, 0°C, 7 min	 **4** (75%) + **5**[a]

[a] ca. of 10%, determined by GC, in the crude product.

Keywords: oxidation; thallium trinitrate; ring contraction; indans.
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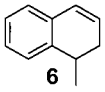
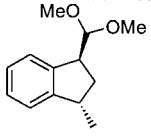
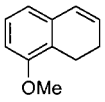
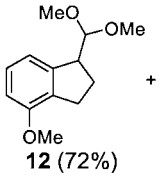
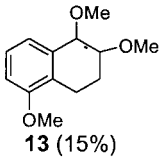
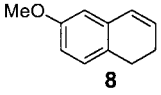
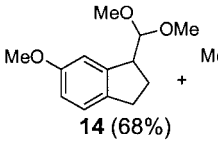
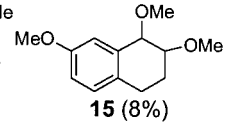
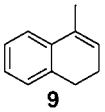
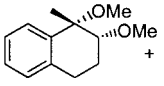
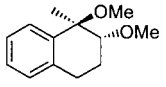
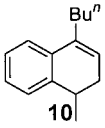
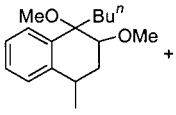
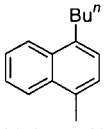
PII: S0040-4020(00)01174-1

Table 2. Reaction of 1,2-dihydronaphthalenes with TTN

Entry	Substrate	Conditions	Product (yield)	
1	 **6**	MeOH, 0 °C, 5 min	 **11** (87%)	
2	 **7**	MeOH, 0 °C, 5 min	 **12** (72%)	 **13** (15%)
3	**7**	TMOF, 0 °C, 5 min	**12** (77%)	**13** (10%)
4	 **8**	MeOH, 0 °C, 5 min	 **14** (68%)	 **15** (8%)
5	**8**	TMOF, 0 °C, 5 min	**14** (74%)	**15** (6%)
6	 **9**	MeOH, -30 °C, 15 min	 **16a** (38%)	 **16b** (31%)
7	 **10**	MeOH, rt, 40 min	 **17** (23%)	 **18** (*ca.* 5%)

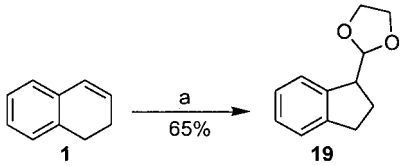
product ratio was observed. Nevertheless, running the reaction of **7** and **8** with TTN in trimethylorthoformate (TMOF) at 0°C, made it possible to increase the ratio of ring contraction product to glycolic derivative (entries 3 and 5).

Contrary to the aforementioned examples, substrates possessing trisubstituted double bonds did not undergo ring contraction. Thus, naphthalene **9** gave rise to the dimethoxylated diols **16a** and **16b**, while **10** led to **17** and **18**, together with significant amounts of unidentified by-products (entries 6 and 7). These results are somewhat unexpected, because the ring contraction of other olefins bearing an alkyl group at the double bond has already been described.[3,5,11,14] An alternative method for performing the ring contraction of **1** and **9** has been recently described by Hara et al.[15] using *p*-Tol-IF_2. The naphthalene derivative **18** is presumably formed through an allylic oxidation of **10**, followed by elimination. It is noteworthy that the allylic oxidation of cyclohexene promoted by thallium(III) salts has been reported in diverse works.[11,16,17]

Finally, the methodology described above showed to be useful for directly access a dioxolane derivative. Thus, the reaction of **1** with TTN in ethyleneglycol furnished **19** as a single product, in 65% yield as shown in Scheme 1.

In conclusion, this work shows that TTN can efficiently promote the ring contraction of 1,2-dihydronaphthalenes—exceptions are substrates possessing trisubstituted double bonds—leading to functionalized indans in very good yields.

Herein is demonstrated one more example that thallium (III)-mediated ring contraction can be an interesting tool



Scheme 1. a: TTN·$3H_2O$, $HOCH_2CH_2OH$, room temperature 15 min.

to construct cyclopentane moities from readily available and inexpensive six-membered ring substrates.

1. Experimental

Warning. Thallium salts are toxic and must be handled with care.

Substrates **1**, **6**, **7** and **8** were prepared from the corresponding commercially available 1-tetralones, by reduction with $NaBH_4$ (or $LiAlH_4$) followed by dehydration with H_3PO_4. The naphthalenes **9** and **10** were obtained through Grignard reaction of 1-tetralone and 4-methyl-1-tetralone, respectively, followed by HCl in situ dehydration. Thallium(III) nitrate was purchased from Aldrich and was used as received. Column chromatography was performed using silica gel Acros 230-400 mesh. TLC analyses were performed with silica gel plates Merck, using vanilline solution for visualization. ^1H and ^{13}C NMR spectra were recorded on Bruker spectrometers. IR spectra were measured on a Perkin–Elmer 1750-FT. Gas chromatography analyses were performed in a HP-6890 series II.

1.1. General procedure for the oxidation of 1,2-dihydronaphthalenes with TTN

To a stirred solution of **1** (0.213 g, 1.64 mmol) in MeOH (5 mL) was added TTN·$3H_2O$ (0.80 g, 1.1 mmol) at 25°C. The reagent promptly dissolved. The mixture was stirred for 1 min and an abundant precipitation was observed. The resulting suspension was filtered through a silica gel pad (70-230 mesh, ca. 10 cm), using CH_2Cl_2 as eluent. The filtrate was washed with H_2O, with brine and dried over anhydrous $MgSO_4$. The solvent was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel 230-400 mesh, gradient elution, 0–50% EtOAc in hexanes), affording **2** (0.189 g, 0.983 mmol, 60%), **3a**[18] (0.010 g, 0.052 mmol, 3%) and **3b**[18] (0.017 g, 0.088 mmol, 5%). 1,1-Dimethoxymethylindane (**2**): colorless oil; IR (film): 2949, 2937, 2829, 1191, 1153, 1123, 1097, 1078, 1058, 750 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.87–2.05 (m, 1H), 2.10–2.28 (m, 1H), 2.74–3.02 (m, 2H), 3.36 (s, 3H), 3.42 (s, 1H), 3.40–3.51 (m, 1H), 4.33 (d, J=7.4 Hz, 1H), 7.12–7.20 (m, 3H), 7.41 (t, J=4.4 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.3, 31.3, 47.4, 52.8, 54.1, 107.1, 124.3, 125.4, 126.0, 126.8, 142.7, 144.7; MS *m/z* (%) 192 (M^+, 0.7), 161 (11), 129 (17), 115 (22), 91 (8), 75 (100), 63 (4), 47 (24). HRMS Calcd for $C_{12}H_{16}O_2$ 192.1150, found 192.1149. In an analogous preparation, a mixture of **1** (0.118 g, 0.906 mmol), MeOH (6 mL) and TTN·$3H_2O$ (0.44 g, 1.0 mmol) was stirred for 5 min at 0°C, to afford **2** (0.133 g, 0.692 mmol, 77%).

1.1.1. 1,1-Diethoxymethylindane (4). A mixture of **1** (0.115 g, 0.883 mmol), EtOH (5 mL) and TTN·$3H_2O$ (0.43 g, 0.97 mmol) was stirred for 7 min at 0°C. Purification by flash chromatography (gradient elution, 0–10% EtOAc in hexanes) gave **4** (0.145 g, 0.658 mmol, 75%) as a colorless oil; IR (film): 2974, 2930, 2884, 1634, 1117, 1062 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.12 (t, J=7.0 Hz, 3H), 1.19 (t, J=7.0 Hz, 3H), 1.90–2.01 (m, 1H), 2.09–2.16 (m, 1H), 2.72–2.79 (m, 1H), 2.84–2.90 (m, 1H), 3.38 (q, J=7.4 Hz, 1H), 3.42–3.50 (m, 2H), 3.57–3.65 (m, 1H), 3.66–3.72 (m, 1H), 4.37 (d, J=7.5 Hz, 1H), 7.00–7.14 (m, 3H), 7.36–7.37 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.3, 15.4, 27.5, 31.4, 48.3, 61.1, 62.4, 105.5, 124.3, 125.6, 126.0, 126.8, 143.1, 144.9; MS *m/z* (%) 220 (M^+, 0.02), 175 (14), 147 (10), 129 (19), 117 (46), 103 (100), 91 (15), 75 (82), 65 (5), 47 (98). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.30; H, 8.96.

1.1.2. *trans*-1,1-Dimethoxymethyl-3-methyl-2,3-dihydro-1*H*-indene (11). A mixture of 1-methyl-1,2-dihydronaphthalene[19] (0.113 g, 0.784 mmol), TTN·$3H_2O$ (0.38 g, 0.86 mmol) and MeOH (6 mL) was stirred for 5 min at 0°C, affording **11** (0.139 g, 0.670 mmol, 85%) as a colorless oil; IR (film): 2957, 2923, 2869, 2830, 1477, 1459, 1374, 1192, 1125, 1101, 1060, 987, 754 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.24 (d, J=6.5 Hz, 3H), 1.69–1.83 (m, H), 2.22–2.34 (m, 1H), 3.20–3.27 (m, 1H), 3.33 (s, 3H), 3.38 (s, 3H), 3.44–3.50 (m, 1H), 4.26 (d, J=7.4 Hz, H), 7.13–7.38 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.5, 36.2, 37.7, 46.2, 52.8, 54.4, 107.0, 123.2, 125.6, 126.1, 127.0, 142.2, 149.3; MS *m/z* (%) 206 (M^+, 0.05), 175 (4), 159 (2), 143 (5), 128 (6),115 (8), 91 (5), 75 (100), 63 (1), 47 (11). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.42; H, 8.54.

1.1.3. Reaction of 8-methoxy-1,2-dihydronaphthalene (7) in MeOH at 0°C. A mixture of **7**[20] (0.150 g, 0.934 mmol), TTN·$3H_2O$ (0.46 g, 1.0 mmol) and MeOH (5 mL) was stirred for 5 min at 0°C. Purification by flash chromatography (10% EtOAc in hexanes), gave **12** (0.150 g, 0.673 mmol, 72%) and **13** (0.0306 g, 0.138 mmol, 15%). 1,1-Dimethoxymethyl-4-methoxy-2,3-dihydro-1*H*-indene (**12**): colorless oil; IR (film): 2942, 2834, 1633, 1593, 1474 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.92–2.28 (m, 2H), 2.68–2.99 (m, 2H), 3.35 (s, 3H), 3.41 (s, 3H), 3.80 (s, 2H), 3.44–3.52 (m, 1H), 4.31 (d, J=7.4 Hz, 1H), 6.69 (d, J=7.3 Hz, 1H), 7.01–7.18 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.9, 27.8, 47.9, 52.8, 54.1, 55.0, 107.1, 108.3, 117.7, 127.5, 132.3, 144.7, 155.7; MS *m/z* (%) 222 (M^+, 2), 191 (8), 159 (6), 147 (7), 131 (2),115 (9), 103 (4), 91 (6), 75 (100), 63 (2), 47 (16). 1,2,5-Trimethoxy-1,2,3,4-tetrahydronaphthalene (**13**): colorless oil; IR (film): 2934, 2893, 2828, 1589, 1466 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.79–2.11 (m, 2H), 2.64–2.72 (m, 2H), 3.44 (s, 3H), 3.50 (s, 3H), 3.66–3.73 (m, 1H), 3.79 (s, 3H), 4.25 (d, J=5.1 Hz, 1H), 6.74 (d, J=8.1 Hz, 1H), 6.97 (d, J=7.3 Hz, 1H), 7.13–7.23 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.4, 22.5, 55.2, 56.5, 57.3, 77.6, 79.4, 108.8, 121.8, 125.7, 126.3, 135.6; MS *m/z* (%) 222 (M^+, 11), 190 (24), 164 (100), 149 (58), 134 (10),115 (20), 105 (7), 91 (40), 77 (16), 65 (10), 45 (13). HRMS Calcd for $C_{13}H_{18}O_3$ 222.1256, found 222.1255.

1.1.4. Reaction of 8-methoxy-1,2-dihydronaphthalene (7) in MeOH at −78°C. A mixture of **7**[20] (0.127 g, 0.794 mmol), TTN·$3H_2O$ (0.39 g, 0.87 mmol) and MeOH (6 mL) was stirred for 30 min at −78°C and 5 min at room temperature. Purification by column chromatography gave **12** (0.077 g, 0.35 mmol, 44%) and **13** (0.023 g, 0.10 mmol, 13%).

1.1.5. 1,1-Dimethoxymethyl-4-methoxy-2,3-dihydro-1*H*-indene (12). A mixture of **7**[20] (0.113 g, 0.705 mmol), TTN·$3H_2O$ (0.35 g, 0.78 mmol) and TMOF (3.5 mL) was stirred for 5 min at 0°C. Purification by flash chromatography (10% EtOAc in hexanes) gave **12** (0.120 g, 0.540 mmol, 77%) and **13** (0.015 g, 0.069 mmol, 10%).

1.1.6. Reaction of 6-methoxy-1,2-dihydronaphthalene (8) in MeOH. A mixture of **8**[20] (0.123 g, 0.768 mmol), TTN·$3H_2O$ (0.38 g, 0.85 mmol) and MeOH (4 mL) was stirred for 5 min at 0°C. Purification by flash chromatography (gradient elution, 10–20% EtOAc in hexanes) gave **14** (0.116 g, 0.522 mmol, 68%) and **15** (0.014 g, 0.063 mmol, 8%). 1-Dimethoxymethyl-6-methoxy-2,3-dihydro-1*H*-indene (**14**): colorless oil; IR (film): 2940, 1709, 1612, 1492, 1281 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.87–2.05 (m, 1H), 2.11–2.29 (m, 1H), 2.68–2.95 (m, 2H), 3.36 (s, 3H), 3.40 (m, 1H), 3.43 (s, 3H), 3.77 (s, 3H), 4.31 (d, J=7.3 Hz, 1H), 6.73 (dd, J=2.2 and 8.5 Hz, 1H), 7.01 (d, J=2.2 Hz, 1H), 7.09 (d, J=8.8 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.8, 30.3, 47.5, 52.5, 54.0, 55.2, 107.0, 110.9, 112.6, 124.5, 136.6, 158.4; MS *m/z* (%) 222 (M^+, 6), 191 (9), 159 (8), 147 (9), 131 (3),115 (9), 103 (5), 91 (6), 75 (100), 63 (2), 47 (16). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 69.87; H, 7.86. 1,2,7-Trimethoxy-1,2,3,4-tetrahydronaphthalene (**15**): colorless oil; IR (film): 2934, 2831, 1613, 1501, 1463, 1264, 1250, 1110, 1087 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.73–1.96 (m, 1H), 2.04–2.19 (m, 1H), 2.62–2.87 (m, 1H), 3.46 (s, 3H), 3.53 (s, 3H), 3.67–3.74 (m, 1H), 3.79 (m, 1H), 4.24 (d, J=5.2 Hz, 1H), 6.77 (dd, J=2.9 and 8.1 Hz, 1H), 6.90 (d, J=2.2 Hz, 1H), 7.02 (d, J=8.1 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.9, 24.8, 55.3, 57.5, 78.0, 80.1, 114.0, 114.2, 129.0, 129.4, 135.7, 157.8.

1.1.7. 1,1-Dimethoxymethyl-6-methoxy-2,3-dihydro-1*H*-indene (14). A mixture of **8**[20] (0.141 g, 0.768 mmol), TTN·$3H_2O$ (0.43 g, 0.97 mmol) and TMOF (4.5 mL) was stirred for 5 min at 0°C. Purification by flash chromatography (gradient elution, 10–20% EtOAc in hexanes) gave **14** (0.144 g, 0.648 mmol, 74%) and **15** (0.013 g, 0.057 mmol, 6%).

1.1.8. Reaction of 4-methyl-1,2-dihydronaphthalene (9) with TTN at −30°C. A mixture of **9**[21] (0.039 g, 0.27 mmol), TTN·$3H_2O$ (0.21 g, 0.47 mmol) and MeOH (5 mL) was stirred for 15 min at −30°C. Purification by column chromatography gave **16a** (0.021 g, 0.10 mmol, 38%) and **16b** (0.017 g, 0.082 mmol, 31%). *cis*-1,2-Dimethoxy-1-methyl-1,2,3,4-tetrahydronaphthalene (**16a**): colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ 1.47 (s, 3H), 1.69–1.90 (m, 1H), 2.20–2.34 (m, 1H), 2.87 (q, J=4.4 Hz, 2H), 3.06 (s, 3H), 3.53 (s, 3H), 3.74 (dd, J=3.7 and 7.0 Hz, 1H), 7.05–7.26 (m, 3H), 7.42–7.47 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.5, 24.7, 28.0, 50.1, 57.1, 58.8, 77.6, 80.1, 126.2, 126.4, 128.2, 136.5, 139.6. *trans*-1,2-Dimethoxy-1-methyl-1,2,3,4-tetrahydronaphthalene (**16b**): colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ 1.54 (s, 3H), 1.91–2.06 (m, 1H), 2.11–2.29 (m, 1H), 2.65–2.80 (m, 1H), 2.95–3.11 (m, 1H), 3.21 (s, 3H), 3.46 (s, 3H), 3.47 (dd, J=3.2 and 8.3 Hz, 1H), 7.07–7.12 (m, 1H), 7.14–7.22 (m, 2H), 7.44–7.52 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.0, 23.0, 26.2, 50.9, 76.1, 81.9, 125.5, 127.1, 127.2, 128.6, 136.2, 138.5.

1.1.9. Reaction of 4-*n*-butyl-1-methyl-1,2,3,4-tetrahydronaphthalene (10) with TTN at 25°C. A mixture of **10** (0.071 g, 0.35 mmol), TTN·$3H_2O$ (0.17 g, 0.38 mmol) and MeOH (6 mL) was stirred for 40 min at room temperature. Purification by column chromatography gave **17** (0.021 g, 0.085 mmol, 23%) and **18**. 1-*n*-Butyl-1,2-dimethoxy-4-methyl-1,2,3,4-tetrahydronaphthalene (**17**): colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, J=7.0 Hz, 3H), 0.96–1.42 (m, 2H), 1.38 (d, J=7.0 Hz, 3H), 1.83–2.23 (m, 6H), 2.83–2.95 (m, 1H), 3.08 (s, 3H), 3.46 (s, 3H), 3.47 (dd, J=3.8 and 11.3 Hz, 1H), 7.15–7.40 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 22.9, 23.2, 26.5, 30.0, 31.9, 32.2, 50.7, 57.1, 78.6, 79.6, 125.2, 127.6 (2x), 134.9, 142.7. 1-*n*-Butyl-4-methylnaphthalene[22,23] (**18**): colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ 0.96 (t, J=7.0 Hz, 3H), 1.39–1.76 (m, 5H), 2.67 (s, 3H), 3.04 (t, J=7.3 Hz, 2H), 7.24 (d, J=7.3 Hz, 2H), 7.47–7.55 (m, 2H), 7.99–8.09 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 19.4, 22.9, 32.8, 33.1, 124.5, 124.8, 125.1, 125.2, 125.5, 126.3, 131.9, 132.2, 137.1.

1.1.10. 1-Dioxolanyl-2,3-dihydro-1*H*-indene (19). A mixture of **1** (0.267 g, 2.05 mmol), TTN·$3H_2O$ (1.00 g, 2.26 mmol) and diethyleneglycol (5 mL) was stirred for 15 min at room temperature, affording pure **19** (0.254 g, 1.34 mmol, 65%) as a colorless oil; IR (film): 2947, 2885, 1478, 1131, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.05–2.12 (m, 1H), 2.17–2.30 (m, 1H), 2.81–3.05 (m, 2H), 3.37–3.43 (m, 1H), 3.84–3.98 (m, 4H), 4.97 (d, J=5.3 Hz, 1H), 7.15–7.23 (m, 3H), 7.40–7.43 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.7, 31.6, 48.9, 64.9, 65.3, 106.6, 124.5, 125.4, 126.1, 127.1, 142.1, 144.9; MS, *m/z* (%) 190 (M^+, 2), 129 (3), 115 (16), 91 (5), 73 (100). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.70; H, 7.37.

Acknowledgements

The authors wish to thank FAPESP, CNPq and CAPES for financial support. We also thank Matthew Tremblay for his careful help with the text and Prof. Carlos R. D. Correia for his help in carrying out the HRMS.

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