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Influence of Electron Donating Aromatic Substituents on the Ruthenium Tetroxide-Catalysed Oxidation of (±)-Podocarpa-8,11,13-trienes

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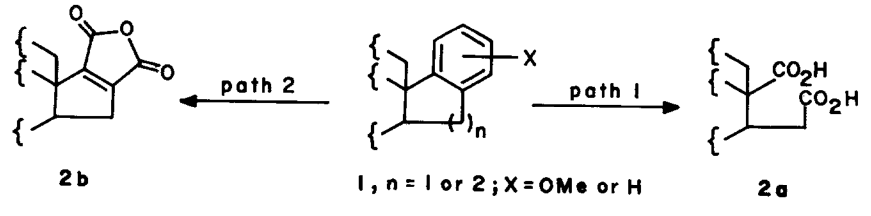
Abstract : Whereas the (±)-podocarpa-8,11,13-trienes **3b-e**, incorporating a phenolic hydroxyl or methyl ether functionality at C-11 and C-14, and C-14 respectively, on oxidation with sodium metaperiodate - catalysed by ruthenium tetroxide give (±)-winterin, through chemoselective degradation of the aromatic ring, the unsubstituted **3a**, isomeric methyl ethers **3f-i**, and cis-podocarpa-8,11,13-triene undergo only benzylic oxidation resulting in the respective ketones **8d**, **8a-c**, **8e** and the diketone **9**. Similar oxidation reaction of the hexahydrophenanthrene **7a** led to the α,β-unsaturated tricyclic ketone **11a** and the tetrahydronaphthalene dicarboxylic anhydride **12**. In contrast, **7b** produced the diketone **10b** and the α,β-unsaturated ketone **11b** as the sole isolated products.

The periodate - based ruthenium tetroxide - catalysed oxidative degradation of aromatic rings to carboxylic acids[1] is an attractive alternative to the exhaustive ozonolysis method.[2] In general, terminating sites in such oxidations,[1e,3,4] in fused hydroaromatic system **1**, correspond to carbon-carbon aromatic bonds adjacent to carbon-carbon single bonds containing an sp^3 centre, resulting in the respective dicarboxylic acids **2a** (Scheme 1, path 1). The alternative possibility of the partial degradation of the aromatic ring in **1** leading to dicarboxylic acids **2b** (or the respective anhydrides) (path 2) is known only for polynuclear aromatic compounds.[1f,h]

Scheme I

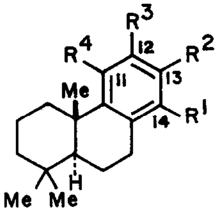


A partial synthesis[5] of (±)-winterin **4** was achieved through oxidative degradation by ozonolysis of the aromatic ring of the (+)-podocarpatriene hydroquinone **3b**, prepared by a lengthy sequence of reactions from (+)-podocarpic acid. Similar transformations of (+)-podocarpic acid and (+)-abietane derivatives to a few other drimane sesquiterpenoids were also reported[6]. Recently, (+)-royleanone **5a** has been converted[7] to (+)-**4**, in low yield, using Hooker's oxidation of the quinone ring as the key step.

In continuing our work[3,4] on the periodate - based ruthenium catalysed oxidative degradations of aromatic rings in fused hydroaromatic systems, we turned our attention to explore such reagents on a large number of readily available (±)-podocarpa-8,11,13-triene derivatives, recently reported by us.[8,9] Of particular interest of this study was to develop a simple preparative route to (±)-winterin **4**,[10] a potential intermediate towards some antifeedant drimane analogous.[11] We describe in this paper the results of our oxidation study on the unsubstituted and the electron donating aromatic ring oxygenated podocarpatrienes[8,9] **3a**, **3b-i** and **6** along with the related hexahydrophenanthrene derivatives **7a**[12] and **7b**.[13]

Results and Discussion

Preliminary oxidation experiments on the hydroquinone **3b** or the dimethoxy compound **3c** using a ligand bound ruthenium reagent,[3] *cis*-$[Ru(bpy)_2Cl_2].2H_2O$ (bpy = 2,2'-bipyridine) catalyst and $NaIO_4$ as the primary oxidant, under several reaction conditions,[3] led to intractable products. The procedure, which turned out to be the most satisfactory for the oxidations of the podocarpatrienes and the other substrates investigated in the present work, was based upon the oxidation with RuO_4, generated from a catalytic amount of $RuCl_3.XH_2O$ in $MeCN-CCl_4-H_2O$ solvent system with $NaIO_4$ at room temperature according to Sharpless.[14] Thus, oxidation of **3b** and **3c** directly afforded (±)-winterin **4**[10] in 60% and 55% yields respectively, as the only isolable product. The oxidation of the phenol **3d** and the respective ether **3e** yielded **4** in 55% and 45% yields respectively, by smooth degradation of the aromatic ring, possibly through the initial formation of the quinone intermediate **5b**. Under similar conditions, however, the isomeric dimethoxy , methoxy and the desmethoxy podocarpatrienes **3f**, **3g**, **3h** and **3a** gave the respective ketones **8a**, **8b**, **8c** and **8d** in good to excellent yields. Similar benzylic oxidation with this reagent has been reported[1e,15] with other substrates. The *o*-dihydroxy compound **3i** gave (±)-nimbidiol **8e**[8] in 35% yield as the only isolable product. The oxidation of the *cis*-dimethoxy compound **6** afforded the diketone **9**[8] in good yield, which is parallel to that observed in chromic acid oxidation.[8,16]



3a ; $R^1 = R^2 = R^3 = R^4 = H$

3b ; $R^1 = R^4 = OH$; $R^2 = R^3 = H$

3c ; $R^1 = R^4 = OMe$; $R^2 = R^3 = H$

3d ; $R^1 = OH$; $R^2 = R^3 = R^4 = H$

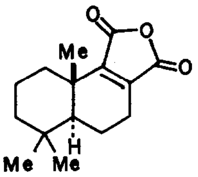
3e ; $R^1 = OMe$; $R^2 = R^3 = R^4 = H$

3f ; $R^1 = R^4 = H$; $R^2 = R^3 = OMe$

3g ; $R^1 = R^3 = OMe$; $R^2 = R^4 = H$

3h ; $R^1 = R^2 = R^4 = H$; $R^3 = OMe$

3i ; $R^1 = R^4 = H$; $R^2 = R^3 = OH$



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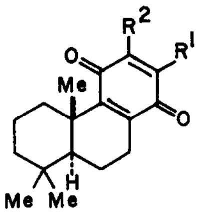
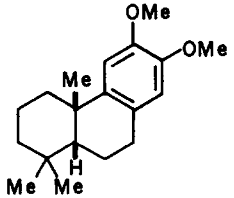


5a ; $R^1 = iPr$; $R^2 = OH$

5b ; $R^1 = R^2 = H$



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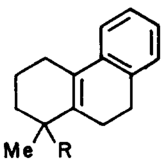
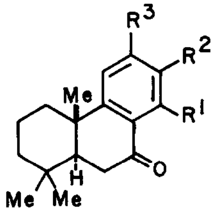


7a ; R = Me

7b ; $R = CO_2Me$



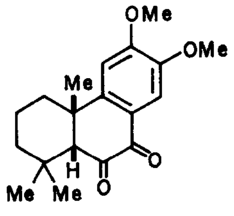
8a ; $R^1 = H$; $R^2 = R^3 = OMe$

8b ; $R^1 = R^3 = OMe$; $R^2 = H$

8c ; $R^1 = R^2 = H$; $R^3 = OMe$

8d ; $R^1 = R^2 = R^3 = H$

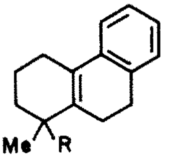
8e ; $R^1 = H$; $R^2 = R^3 = OH$



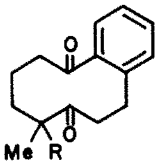
9

To evaluate the relative susceptibilities of the different reactive sites in RuO$_4$-catalysed oxidation of the hexahydrophenanthrenes 7a and **7b**, we investigated these substrates. The oxidation of **7a** gave a complex mixture of products, from which the tricyclic α,β-unsaturated ketone **11a** and the anhydride **12** were isolated in 17% and 14% yields respectively.

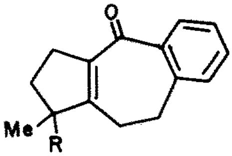
The anhydride **12** was further characterised through the respective dimethyl ester **13**. While the α,β-unsaturated ketone **11a** evidently arises from the intramolecular aldol condensation and dehydration of the intermediate diketone **10a**, the oxidative cleavage product of the tetrasubstituted double bond[17] in **7a**, the anhydride **12** was shown to be an aromatic ring degradation product of the intermediate tetrahydrophenanthrene **14** formed by oxidative dehydrogenation. This was proved by the direct oxidation of **14**[12] affording the anhydride in 70% yield.



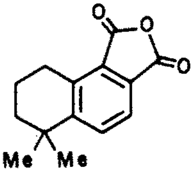
7a ; R = Me
7b ; R = CO_2Me



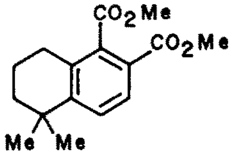
10a ; R = Me
10b ; R = CO_2Me



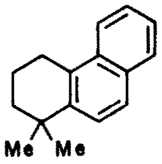
11a ; R = Me
11b ; R = CO_2Me



12



13



14

Interestingly, the hexahydrophenanthrene ester **7b**[13], on oxidation gave a mixture of the diketoester **10b** and the respective cyclised product **11b** in 20% and 23% isolable yields. The diketoester **10b** on intramolecular aldol condensation with methanolic hydrochloric acid gave the cyclised product **11b**, in excellent yield. The tricyclic ketones **11a** and **11b**, incorporating a hydrazulene system, are potential intermediates for the synthesis of grayanotoxins.[18]

In conclusion, the present study provided evidence that oxidation with periodate-based RuO_4-catalysed reaction may occur either in the aromatic ring or at the benzylic position depending on the position of the electron donating oxygen substituent(s) in the aromatic ring of the podocarpa-8,11,13-trienes. The oxygen functionality at C-11 and C-14 or even at C-14 in podocarpatrienes favour selective aromatic ring oxidation giving rise to an anhydride (Scheme 1, path 2), whereas oxygen substitution at C-12 or deoxygenated substrates favour benzylic attack only leading to the respective ketones. These finding should enhance the value and the use of RuO_4-catalysed oxidation as a replacement for ozonolysis in selective transformations of easily accessible hydroaromatic compounds to polyfunctional molecules of importance.

Experimental

The compounds described are all racemates. M.p.s. and b.p.s. are not corrected. IR spectra of solids (KBr) and liquids (film) were recorded on a Perkin-Elmer model PE 298 instrument. UV spectra were recorded on a Beckman DU spectrometer for solution in ethanol (95%). ^{1}H NMR spectra were recorded at 200 MHz on an XL-200 spectrometer for solution in $CDCl_3$ with $SiMe_4$ as internal standard. J. values are given in Hz. Analytical GLC was performed on a Shimadzu GC-9A model with flame-ionisation detector employing a 1.5% OV-17 (6.5 ft x 0.25 in) column with N_2 as the carrier gas. The mass spectra were recorded on a VG-micromass 7070H mass spectrometer or a Jeol-DX 303 GC mass spectrometer. Column chromatography was performed on neutral alumina (Brockmann Grade 1, of BDH, India). Petroleum ether refers to the fraction of b.p. 60-80°C unless otherwise mentioned. Ether refers to diethyl ether.

Oxidation of 3b-e to (±)-Winterin 4.

Oxidation of 3b to 4. - To a deep violet magnetically stirred solution of $RuCl_3.3H_2O$ (26.1 mg, 0.1 mmol) and the (±)-11,14-dihydroxypodocarpatriene **3b** (500 mg, 1.92 mmol) in acetonitrile (5 ml) and carbon tetrachloride (5 ml) at 25-30°C, a solution of sodium metaperiodate (1.6 g, 7.68 mmol) in water (7.5 ml) was added. After ca. 10-20 min the colour of the reaction mixture turned to dark orange-red. The stirring at room temperature (ca. 25-30°C) was continued for 15 h, by which time the starting material had disappeared (t.l.c.). The mixture was diluted with water (8 ml) and extracted with ether (4 x 20 ml). The combined organic extracts were washed with saturated aqueous sodium chloride (10 ml), 3% aqueous sodium thiosulphate (2 x 5 ml), saturated aqueous sodium chloride (10 ml) and dried (Na_2SO_4). Removal of the solvent under reduced pressure afforded the crude product, which was chromatographed over neutral alumina (15 gm). Elution with petroleum ether-ethyl acetate (10:1) (10 x 40 ml) afforded (±)-winterin **4** (276 mg, 60%), m.p. 153-154°C (from methanol) (lit[10] m.p. 153-155°C); ν_{max}/cm^{-1} 1838, 1765 and 1665; δ 0.93 (3H, s, Me), 0.96 (3H, s, Me), 1.04-2.40 (9H, m), 1.28 (3H, s, 10-Me), 2.64-2.80 (2H, m, 7-H_2).

Oxidation of 3c to 4. - The compound **3c** (500 mg, 1.74 mmol) was converted in the same way as described above into the compound **4** (237 mg, 55%), identical (IR, GLC and ^{1}H NMR spectra) with the sample described above.

Oxidation of 3d to 4. - The compound **3d** (500 mg, 2.04 mmol) was converted in the same way as described above into the compound **4** (278 mg, 55%), identical (IR, GLC and ^{1}H NMR spectra) with the sample described above.

Oxidation of 3e to 4. - The compound **3e** (500 mg, 1.93 mmol) was converted in the same way as described above into the compound **4** (216 mg, 45%), identical (IR, GLC and ^{1}H NMR spectra) with the sample described above.

Oxidation of 3a, 3f-i and 6.

Oxidation of 3a to 3d. - Compound **3a** (500 mg, 2.18 mmol), sodium metaperiodate (2.01 g, 9.4 mmol), $RuCl_3.3H_2O$ (26.1 mg, 0.1 mmol), carbon tetrachloride (5 ml), acetonitrile (5 ml) and 7.5 ml of water was stirred at room temperature (ca. 20-25°C). After 15 min the colour of the reaction mixture turned to orange-red. The stirring at room temperature was continued for 15 h, by which time the starting material had disappeared (t.l.c.). The mixture was diluted with water (8 ml) and extracted with ether (4 x 20 ml). The combined organic extracts were washed with saturated aqueous chloride (10 ml), 3% aqueous sodium thiosulphate (2 x 5 ml), saturated aqueous sodium chloride (10 ml) and dried (Na_2SO_4). Removal of the solvent under reduced pressure afforded the crude product. The crude product was chromatograph over neutral alumina (15 g), elution with petroleum ether-ethylacetate (10:1) (7 x 35 ml) afforded **8d** (397 mg, 75%), b.p. 142-145°C (1 mmHg) (lit[19], described as an oil); ν_{max}/cm^{-1} 1685 and 1600; δ 0.93 (3H, s, Me), 1.04 (3H, s, Me), 1.08-3.00 (9H, m), 1.26 (3H, s, 10-Me), 7.10-7.70 (3H, m, 11,12 and 13-ArH), 8.12 (1H, d, J = 8,14-ArH).

Oxidation of 3f to (±)-Nimbidioldimethylether 8a - Compound **3f** (500 mg, 1.73 mmol) was converted, in the same way as described for **8d**, into the ketone **8a** (286 mg, 55%); identical (IR, GLC and ^{1}H NMR) with an authentic sample.[8]

Oxidation of 3g to (±)-12,14-Dimethoxy-7-oxopodocarpa-8,11,13-triene 8b. - The compound **3g** (500 mg, 1.73 mmol) was converted, in the same way as described for **8d**, into the ketone **8b** (286 mg, 55%), m.p. 138°C (chloroform-petroleum ether ν_{max}/cm^{-1} 1675 and 1605; δ 0.96 (3H, s, Me), 0.99 (3H, s, Me), 1.04-3.04 (9H, m), 1.24 (3H, s, 10-Me), 3.85 (3H, s, ArOMe), 3.92 (3H, s, ArOMe), 6.35 (1H, br s, 11-ArH), 6.54 (1H, br s, 13-ArH). Found : C, 75.50; H, 8.50. Calc. for $C_{19}H_{26}O_3$ C, 75.46; H, 8.67%;

Oxidation of 3h to 8c. - The compound **3h** (500 mg, 1.93 mmol) was converted, in the same way as described for **8d**, into the ketone **8c** (394 mg, 75%), b.p. 135-140°C (1 mmHg) (lit.[19], described as an oil); ν_{max}/cm^{-1} 1685 and 1600; δ 0.94 (3H, s, Me), 1.01 (3H, s, Me), 1.24 (3H, s, 10-Me), 1.04-2.98 (9H, m), 3.75 (3H, s, ArOMe), 6.75-6.90 (2H, m, 11 and 13-ArH), 8.08 (1H, d, J 9.5, 14-ArH).

Oxidation of 3i to (±)-Nimbidiol 8e. - Compound **3i** (500 mg, 1.92 mmol) was converted, in the same way as described for **8d**, into the ketone **8e** (184 mg, 35%), m.p. 223°C, identical (mixed m.p. IR, GLC and ^{1}H NMR) with an authentic sample.[8] m.p. 223°C.

Oxidation of 6 to (±)-5-epi-6-oxonimbidioldimethylether 9. - Oxidation of **6** (500 mg, 1.73 mmol) was converted, in the same way as described for **8d**, into the diketone **9** (272 mg, 50%), m.p. 198°C, identical (mixed m.p., IR, GLC and ^{1}H NMR) with an authentic sample,[8] m.p. 198°C.

Oxidation of 7a to 1,2,3,4,9,10-Hexahydro-1,1-dimethyl-4-oxo benz[f] azulene 11a and 1,2,3,4-Tetrahydro-1,1-dimethylnaphthalene-5,6-dicarboxylic anhydride 12. - Compound **7a** (1 g, 4.70 mmol), sodium metaperiodate (4.02 g, 18.8 mmol), $RuCl_3.3H_2O$ (52.2 mg, 0.2 mmol), carbon tetrachloride (10 ml), acetonitrile (10 ml) and 15 ml of water was stirred at room temperature (ca. 20-25°C) for 15 h. After adding 15 ml of water, the mixture was extracted repeatedly with ether (5 x 20 ml). The combined extracts were washed with water, 3% aqueous $Na_2S_2O_3$, saturated aqueous sodium chloride, and dried (Na_2SO_4). The crude product was chromatographed over neutral alumina (30 g). Elution with petroleum ether afforded starting material **7a** (80 mg, 8%). Elution with ethylacetate - petroleum ether (1:19) (10 x 45 ml) afforded the anhydride **12** (150 mg, 14%), m.p. 121-122°C (from ethanol) ν_{max}/cm^{-1} 1837 and 1772; λ_{max} (EtOH)/nm 223 (log ε 4.35) and 317 (log ε 3.31); δ 1.36 (6 H, s, CMe_2), 1.70-1.80 (2 H, m, 2-H_2), 1.82-1.96 (2 H, m, 3-H_2), 3.25 (2 H, t, J 7, 4-H_2), 7.80 (1 H, d, J 8, ArH), 7.88 (1H, d, J 8, ArH); Found : C, 72.73; H, 5.79. Calc. for $C_{14}H_{14}O_3$ C, 73.02; H, 6.13%; m/z 230 (M^+, 76%), 215 (100), 210 (9), 187 (10), 143 (11), 128 (13) and 115 (10).

Further elution with ethylacetate - petroleum ether (1:9) furnished the conjugated ketone **11a** (200 mg, 17%), b.p. 145-150°C (0.1 mmHg) ν_{max}/cm^{-1} 1625 and 1600; λ_{max} (EtOH)/nm 205 (log ε 4.15), 258 (log ε 3.87) and 282 (log ε 3.93); δ1.11 (6 H, s, CMe_2), 1.70 (2 H, t, J 8, 2-H_2), 2.42-2.80 (4 H, m, 3 and 8-H_2), 2.98-3.06 (2 H, m, 7-H_2), 7.20 (1 H, d, J 8, ArH), 7.27-7.45 (2 H, m, ArH), 7.77 (1 H, br d, ArH); m/z 226 (M^+, 100%), 211 (76), 197 (21), 163 (55), 141 (20), 115 (12), 91 (20), 77 (12), 55 (10) and 41 (9). Found : C, 84.70; H, 8.22. Calc. for $C_{16}H_{18}O$ C, 84.91; H, 8.02%;

Conversion of 12 to 1,2,3,4-Tetrahydro-1,1-dimethyl-5,6-dicarbomethoxynaphthalene 13. - The anhydride **12** (22 mg, 0.08 mmol) was stirred for 5 h at room temperature (ca. 20-25°C) with 5% aqueous NaOH (2 ml). The saponified mixture was acidified with HCl (6N) and extracted with ether (3 x 10 ml). The ethereal extracts were washed with water and dried (Na_2SO_4). The crude diacid (22 mg) obtained after evaporation of the solvent was esterified with an excess of ethereal diazomethane solution to afford **13** (25 mg, 94%), b.p. 150-155°C (0.1 mmHg) ν_{max}/cm^{-1} 1725 and 1600; δ 1.31 (s, 6H, CMe_2), 1.57-1.88 (4 H, m, 2 and 3-H_2), 2.75 (2 H, t, J 6, 4-H_2), 3.92 (3 H, s, $ArCO_2Me$), 3.99 (3 H, s, $ArCO_2Me$), 7.51 (1 H, d, J 8, ArH), 7.85 (1 H, d, J 8, ArH). Found : C, 69.40; H, 7.12. Calc. for $C_{16}H_{20}O_4$ C, 69.54; H, 7.30%;

Oxidation of 14 to 12. - The compound **14** (250 mg, 1.19 mmol) was converted, in the same way as described above into the anhydride **12** (192 mg, 70%), m.p. 122°C, identical (mixed m.p., IR, GLC and ^{1}H NMR spectra) with the sample described above.*

Oxidation of 7b* to Methyl 1,2,3,4,9,10-hexahydro-1-methyl-4-oxo benz[f] azulene-1-carboxylate 11b and Methyl 5,6,7,8,9,10,11,12-octahydro-9-methyl-5,10-dioxo benzocyclodecene-9-carboxylate 10b. - The compound **7b** (1 g, 3.9 mmol) was oxidised in the same way as described for **7a** into the mixture of **11b** and **10b**. The mixture was chromatographed over neutral alumina (30 g) and elution with petroleum ether afforded starting material **7b** (70 mg, 7%). Elution with ethylacetate - petroleum ether (1:9) furnished the compound **11b** (150 mg, 23%), b.p. 150-160°C (0.1 mmHg) ν_{max}/cm^{-1} 1725, 1628 and 1600; λ_{max} (EtOH)/nm 204 (log ε 4.82), 229 (log ε 3.76), 257 (log ε 3.86) and 281 (log ε 3.87); δ 1.39 (3 H, s, Me), 1.70-2.62 (4 H, m, 2 and 8-H_2), 2.78-3.18 (4 H, m, J 7-H_2), 3.72 (3 H, s, -CO_2Me), 7.24 (1 H, br d, ArH), 7.29-7.50 (2 H, m, ArH), 7.78 (1 H, br d, ArH); m/z 270 (M^+, 63%), 211 (100), 195 (12), 163 (54), 170 (12), 141 (15), 126 (8), 115 (9), 91 (14), 77 (9) and 55 (8). Found : C, 75.16; H, 6.79. Calc. for $C_{17}H_{18}O_3$ C, 75.53; H, 6.71%;

On further elution with ethylacetate - petroleum ether (1:4) (7 x 35 ml) afforded **10b** (130 mg, 20%), m.p. 100°C (ethanol) ν_{max}/cm^{-1} 1735, 1710, 1680 and 1600; λ_{max} (EtOH)/nm 218 (log ε 3.68), 244 (log ε 3.51) and 281 (log ε 2.73); δ 1.24 (3 H, s, Me), 1.34-3.12 (8 H, m, 3,8,9 and 10-H_2), 3.25 (2 H, t, J 6, 4-H_2), 3.70 (3 H, s, CO_2Me), 7.24-7.46 (4 H, m, ArH); m/z 288 (M^+, 22%), 270 (27), 236 (22), 226 (27), 211 (27), 188 (100), 163 (34), 159 (56), 145 (55), 131 (69), 101 (79), 77 (35) and 41 (46). Found : C, 69.26; H, 6.98. Calc. for $C_{17}H_{20}O_4$ C, 69.36; H, 6.80%;

Conversion of 10b to 11b. - Diketone **10b** (250 mg, 0.86 mmol) was refluxed with conc. HCl (3 ml) in methanol (30 ml) for 1 h. After the removal of the solvent *in vacuo*, the residue was dissolved in ether and washed with water. The solvent was dried (Na_2SO_4) and removed. After removal of solvent the crude product was filtered through short packed neutral alumina (7 g) column to afford **11b** (175 mg, 75%), identical (IR, GLC and ^{1}H NMR) with the sample described above.

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