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# Facile Synthesis of Both Linear and Angular Triquinanes from The Tricyclo[5.4.0.0$^{1,5}$]undec-9-ene-8,11-dione Efficiently Produced by a Combination of Electro- and Photochemical Reactions

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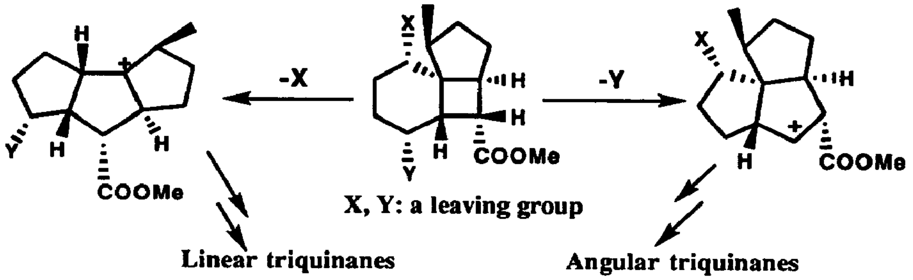
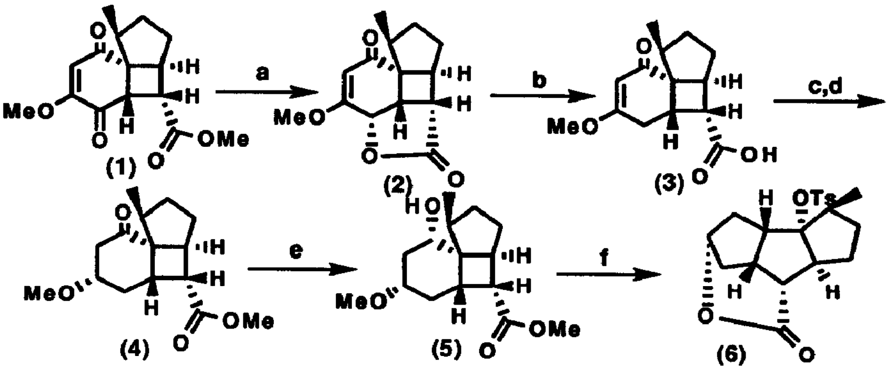
*Abstract:* Both linear and angular triquinanes have been efficiently synthesized from 9-methoxy-6α-methoxycarbonyl-2β-methyltricyclo[5.4.0.0$^{1,5}$]undec-9-ene-8,11-dione.

In the course of our synthetic study on bioactive substances by means of electrochemical methodology,$^{1)}$ we could synthesize 9-methoxy-6α-methoxycarbonyl-2β-methyltricyclo[5.4.0.0$^{1,5}$]undec-9-ene-8,11-dione (1)$^{2)}$ in high yield. This compound 1 is regarded as the common synthetic intermediate for both linear and angular triquinane-type compounds, which are quite attractive because of their structural and biological properties,$^{3)}$ as seen in Scheme 1.



Scheme 1.

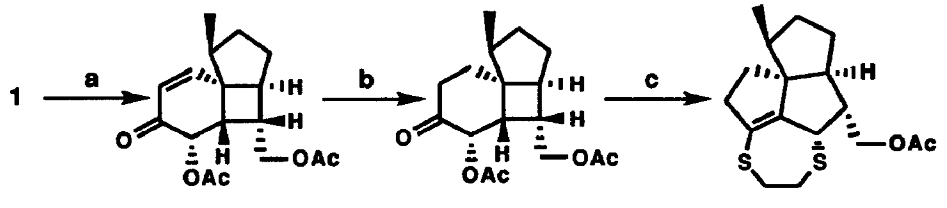


**a) $NaBH_4$ and $CeCl_3$ / MeOH (room temp., 2 h)(70%); b) $H_2$ / Pd-C / EtOAc (room temp., 5.5 h)(90%); c) MeI and $K_2CO_3$ / DMF (room temp., 13 h) (93%); d) $H_2$ / Pd-C / EtOAc (room temp., 3.5 h)(64%); e) $NaBH_4$ / MeOH (room temp., 40 min.)(79%); f) p-TsOH / toluene (refluxing temp., 15 min.) (60%)**

Scheme 2.

On $NaBH_4$ reduction in the presence of $CeCl_3$, the tricyclic compound **1** was readily converted into the lactone **2**,4) in 70% yield, which was further subjected to catalytic hydrogenation to afford **3**,4) in 90% yield. After esterification using MeI and $K_2CO_3$, **3** was hydrogenated again over catalytic amounts of 10% Pd-C to give the corresponding keto-ester (**4**),4) in good yield, which was treated with $NaBH_4$ in MeOH to give **5**,4) in high yield. When treated with p-TsOH in toluene at refluxing temperature for 15 min., **5** was selectively converted into the desired linear triquinane-type compound **6**5) in 60% yield, as seen in Scheme 2. We could also convert the tricyclic compound **1** into the angular triquinane-type compound **7** in short step, as follows.

The tricyclic compound **1** was treated with diisobutylaluminium hydride in THF followed by acetylation resulting in removal of the acetoxyl group at $C_{11}$-position leading to the formation of the α,β-unsaturated ketone **8**,4) in 40% overall yield, which was subjected to catalytic hydrogenation using 10% Pd-C in EtOAc to afford the corresponding saturated ketone **9**,4) in high yield. When treated with 1,2-ethanedithiol and excess $BF_3 \cdot OEt_2$ (1:10) in $CH_2Cl_2$ at room temperature, **9** was readily converted into the desired angular triquinane-type compound **7**5) in 58% yield, as seen in Scheme 3.



**a) 1) DIBAL-H / THF (room temp., 1.5 h), 2) $Ac_2O$ / Pyr. (room temp., 12 h) (40% in 2 steps); b) $H_2$ / 10% Pd-C / MeOH (room temp., 3.5 h) (91%); c) 1,2-ethanedithiol and $BF_3 \cdot OEt_2$ / $CH_2Cl_2$ (room temp., 40 min.) (58%)**

Scheme 3.

The present study indicates a short synthetic pathway leading to both linear and angular triquinane-type sesquiterpenes. Further synthetic studies on a number of highly oxygenated triquinanes are in progress.

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2. Maki, S.; Kosemura, S.; Yamamura, S.; Ohba, S. *Tetrahedron Lett.*, **1993**, *34*, 6083.
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4. The spectral data for the new compounds are in accord with the structures assigned, and the stereochemistry of each compound was elucidated by NOE experiments.
5. **6**: $C_{13}H_{16}O_2$ [m/z 204.1138 ($M^+$ - TsOH)]; IR (film) 1740 $cm^{-1}$; δ ($CDCl_3$) 0.87 (3H, d, J = 6.4 Hz), 1.16 (1H, m), 1.25 - 1.34 (2H, complex), 1.52 - 1.83 (4H, complex), 2.02 (1H, dd, J = 2.0, 15.6 Hz), 2.27 (1H, dd, J = 2.9, 14.2 Hz), 2.45 (3H, s), 2.50 (1H, m), 2.59 - 2.67 (2H, complex), 2.73 (1H, br. s), 4.47 (1H, br. s), 7.34 (2H, d, J = 8.3 Hz), and 7.80 (2H, d, J = 8.3 Hz); **7**: $C_{17}H_{24}O_2S_2$ [m/z 324.1244 ($M^+$)]; IR (film) 1740 $cm^{-1}$; δ ($CDCl_3$) 0.89 (3H, d, J = 5.9 Hz), 1.27 (1H, dd, J = 2.4, 4.9 Hz), 1.30 (1H, dd, J = complex), 2.55 (1H, d, J = 8.8 Hz), 3.05 - 3.20 (5H, complex), 3.92 (1H, dd, J = 7.8, 11.2 H2.4, 4.4 Hz), 1.40 - 1.55 (6H, complex), 1.80 - 1.87 (2H, complex), 2.03 (3H, s), 2.05 - 2.43 (5H, z), and 4.26 (1H, dd, J = 7.3, 11.2 Hz).

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