

Unprecedented Outcome of the Allene Photoaddition to a Fused α,β -Unsaturated Ketone

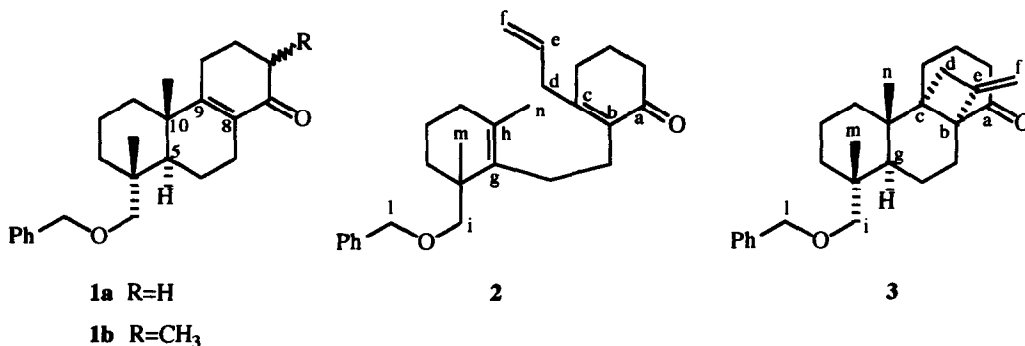
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Abstract: The unprecedented formation, in the course of the allene photoaddition to 18-benzyloxy-8(9)-podocarpene-14-one, of a by-product, due to a novel type of intramolecular hydrogen abstraction by the biradical intermediate, is described.

We have recently¹ described the preparation of 18-benzyloxy-8(9)-podocarpene-14-one **1a**, a key intermediate of our planned total synthesis, by the Wiesner photochemical method,² of the tetracyclic diol stemarin.³

Surprisingly, in the course of the allene photoaddition to **1a** at -78° ,⁴ the adduct **2**^{5,6} was produced in a nearly 1:3 ratio in comparison to the expected cycloadduct **3**⁵.



Compounds **2** and **3** ($R_{12} < R_{13}$) were separated by SiO₂ column chromatography using a 9:1 mixture of *n*-hexane-Et₂O as eluant and a 1:200 substrate/adsorbent ratio.

The structure of compound **2** was established on the basis of its chemical and spectroscopic data⁷ and by comparison of the latter with those of compounds **3**⁸ and **1a**.¹

The formation of **2** can be explained as follows: the initially formed and α configured side chain radical produces, by abstracting the δ H-C(5), a Cope rearrangement like intermediate. Homolytic cleavage of the

C(9)-C(10) bond of the intermediate gives then **2**, the obtaining of which proves also the stereochemistry at C(8) and C(9) of **3**.

Precedents can be found in the literature where, in the course of the addition of unsaturated hydrocarbons to fused α,β -unsaturated ketones, the hydrogen abstraction process prevails or competes with that of cyclization.⁹ Nevertheless the above described case is novel and constitutes a further variant of these processes.

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References and Notes

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4. Irradiations were conducted, while stirring under nitrogen, with a Hg-vapour Helios Italquartz 1000 watt lamp placed in a water cooled Pyrex jacket. The solution of **1a** (41 mg, 0.12 mmoles) and allene (1 ml), in freshly distilled THF (9 ml), was placed in a Pyrex vial, close to the lamp and cooled by means of a dry ice/acetone bath.
5. The elemental composition of all compounds, described in this communication, has been determined by high resolution mass spectrometry.
6. Similar results were obtained when compound **1b** was submitted to allene photoaddition. No compound **2** was formed when pure **3** was irradiated in THF at -78°C .
7. IR (CCl_4): 1670, 1625; ^1H NMR (CDCl_3): 1.04 (s, 3H, m), 1.76 (s, 3H, n), 3.01 (d, 2H, $J=6\text{Hz}$, d), 3.22 and 3.51 (2d, 2H, $J_{\text{AB}}=9\text{Hz}$, i), 4.52 and 4.57 (2d, 2H, $J_{\text{AB}}=13\text{Hz}$, l), 4.95-5.20 (m, 2H, f), 5.76 (m, 1H, e), 7.35 (m, 5H, Ph-); ^{13}C NMR (CDCl_3): 199.3 (a), 155.5 (c), 139.2 (C_{ipso}), 136.7 (h or g) 134.0 (e), 134.0 (h or g), 130.7 (b), 128.2 and 127.4 (C_{ortho} and C_{meta}), 127.1 (C_{para}) 117.0 (f), 76.8 (l), 72.9 (i), 39.5, 39.1, 38.2, 34.3, 32.7, 30.5, 28.5, 25.7, 23.8 (n), 22.4, 20.2, 19.1 (m).
8. IR (CCl_4): 1700; ^1H NMR (CDCl_3): 0.84 (s, 3H, m or n), 0.95 (s, 3H, m or n), 2.91 and 3.19 (2d, 2H, $J=9\text{Hz}$, i), 4.43 and 4.52 (2d, 2H, $J_{\text{AB}}=12\text{Hz}$, l) 4.82 (m, 2H, f), 7.32 (m, 5H, Ph-); ^{13}C NMR (CDCl_3): 212.2 (a), 149.6 (e), 139.2 (C_{ipso}), 128.4, 127.4, 127.4 (C_{ortho} , C_{meta} , C_{para}), 106.0 (f), 79.3 (l), 73.0 (i), 58.1 (b), 49.1, 38.5, 37.9 (g), 37.7, 37.4, 36.4, 35.6, 32.9, 29.3, 27.8, 19.9, 19.3 (m), 17.8, 17.7 (n), 17.5.
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